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NONDESTRUCTIVE REACTIVATION OF CHEMICAL PROTECTIVE GARMENTS

by

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In the near future, chemical protective combat uniforms may be worn by Army personnel on a continuous basis. Activated carbon, the operative component, has diminished capacity for sorbing chemical agents after it has been exposed to dirt, sweat, cigarette smoke, engine exhaust, petroleum products and numerous other elements routinely present in the battlefield environment. This report summarizes the development of two nondestructive methods for cleaning and reactivating soiled chemical protective garments. Complete reactivation was achieved when the aqueous/ i-propanol/ iodine displacement method of Manes, which removed all but pure hydrocarbon oil soils from the current overgarment Type III foam or Kynol activated carbon fiber material, was applied in nonaqueous solvent. Subsequently, a nonaqueous solvent method that requires less handling was chosen in designing a truck-mounted system. It features non-agitative flow of methylene chloride and methanol around the chemical-protective garments suspended between ultrasonic transducers. Both methods restore full sorptivity to the Type III foam liner. There is a one-time 10% loss of activated carbon without any loss of sorptivity. The volatile solvents are more easily removed, and can be economically recovered. Overall features of a mobile unit have been sketched.

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PREFACE

This report summarizes the development and evaluation of methods for reactivation of soiled chemical warfare protective fabric garments and wraps. The initial effort to displace adsorbed soils from activated carbon in the chemical protective layer was based on an aqueous/organic solvent mixture with iodine. The limitations of aqueous systems were addressed in later phases wherein the investigation was directed to development of a sequence of organic solvents with iodine, and also without iodine, and nonagitative procedures that will not cause carbon loss. The development of a refined CCl_4 vapor adsorption test apparatus with Fourier Transform Infrared (FTIR) detector was also undertaken, to make quantitative measurements of the extent of reactivation achieved after the various treatments. The attainment of complete restoration of sorptivity of activated carbon protective material, after heavy soiling with fuel, sweat, smoke, etc., with economy of time and materiel, was the goal. The design of a truck-borne cleaning/reactivation unit utilizing the optimum solvent system, with solvent reclamation, is sketched.

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NONDESTRUCTIVE REACTIVATION OF CHEMICAL PROTECTIVE GARMENTS

SUMMARY

Future chemical protective combat uniforms may be worn on a continuous basis, provided a non-destructive cleaning method can remove not only soils on the fabrics but also the adsorbed soil in the activated carbon. Two methods have been developed by which the sorptive chemical protective suit (MIL-C-43858A GL[1]) can be fully reactivated after heavy exposure to sweat, smoke, gasoline, fuel oil, etc.

During evaluations of various cleaning and reactivation steps applied to soiled material, it became evident that improvement in the test of MIL-C-43858A GL would be necessary. A major effort was required to work out the causes of well-known variability problems in the sorption testing of freshly unpackaged carbon-impregnated polyurethane foam suits, and previously unrecognized interference in starch-iodide detection. Successful correlation of the test with modernized procedures, which will supersede it, was accomplished.

An additional effort addressed the problems arising from ordinary laundering/dry-cleaning methods: the carbon loss caused by agitative laundering and the poisoning of sorptive activity by strongly sorbed dry-cleaning solvent.

The successful resolution of these problems required systematic trials and tests, in the process of which previously unknown effects were discovered. Two of the most striking discoveries were the increase in sorptivity when the impregnated foam was moisturized (and the decrease after oven regeneration[2]), and the ability of a sequence of volatile solvents to remove "poisons" of activated carbon, with the aid of ultrasonic scrubbing.

Some of the alleys of investigation were fruitless: a large microwave activation was realized to be due only to moisture in impregnated foam, when it could not be produced in an activated carbon fiber material (Toyoba Fabric KNF-L-1500)[3]. Aqueous solvent mixtures were only partially successful for removal of hydrocarbon soils, and the entire proposal had to be re-oriented to organic solvents. The original concept of iodine displacement[4] of soil from activated carbon was abandoned in favor of a small organic molecule, dichloromethane, thus eliminating an extra step using aqueous thiosulfate. However, if Cl-compounds are completely banned, the iodine process (in isopropanol, followed by methanol and then aqueous thiosulfate) can be substituted.

The sorptivity of unsoiled, soiled, partially reactivated and fully reactivated samples were evaluated by live agent tests[5] and correlated with equilibrium and dynamic CCl_4 adsorption tests.

Ultrasonic solvent agitation was essential for efficient removal of soils in sequential flows of displacing solvents. The microscrubbing does not ablate impregnated activated carbon from foam material, as occurs with agitation of the fabric in the usual laundering or drying processes. The large system to be mounted on a truck has an array of transducer plates submerged in solvent. The last solvent rinse in methanol completely removes the small displacing molecule, dichloromethane, from activated carbon but does not itself bind, and is volatile, so that it does not require the heat and agitation of ordinary drying methods. Purification of recycling solvent can be accomplished at moderate temperatures.

I. INTRODUCTION

In the near future, a single new uniform, the Chemical Protective Combat Uniform, will be used in lieu of both the Battle Dress Uniform and the chemical protective Battle Dress Overgarment[1]. As an essential requirement, this new uniform must retain chemical protective effectiveness after it has been subjected to laundering, decontamination and regeneration. The primary goal of the present study lies in the development of nondestructive processes by which the active carbon uniform can be reactivated routinely.

Substances adsorbed on activated carbon are bonded in slit-shaped pores by the van der Waals forces acting between the molecules of the substance and the atoms of pore walls. These substances desorb at a rate depending on the bonding strength and on their volatility in air, or solubility in solvent, in liquid systems. The process of desorption of a certain substance can be accelerated by the introduction of another substance having a higher electronic polarizability, which produces stronger van der Waals bonds. This more polarizable substance is called a displacing agent which competes with the originally adsorbed matter for the sorption sites[4]. Due to its stronger bond to the carbon surface, the displacer molecule can remain bound when an originally adsorbed molecule in its vicinity is kicked off by lattice vibrations of the solid. Because migration along the surface is faster than desorption, all sites are quickly filled by the more strongly bound displacer molecules, preventing the return of hovering displaced molecules.

The current chemical protective material, having a liner of activated carbon-impregnated foam, was used as the test substrate in most of the study. In addition, a Toyobo Co. fabric[3] ensemble having a Kynol- activated carbon fiber fabric layer was used in identical fashion, in order to resolve behavior that was unique to the assay tests or to the impregnated foam.

The main objective of the program was that of depositing separately the various representative contaminants on fresh carbon material, applying the appropriate reactivation process, and conducting carbon tetrachloride or chemical agent vapor penetration tests to determine the recovered adsorptive capacity. The cleaning and reactivation process was aimed at complete removal of contaminants from the carbon surface.

Test pieces were thoroughly contaminated with detergent, simulated human sweat, cigarette smoke, gasoline, engine exhaust, diesel fuel, no-lead gasoline, or Freon 113. The contaminated samples were then laundered and reactivated, and dried, using bench-level laboratory techniques.

The initial reactivation method in Phase I used iodine displacement, in aqueous iso-propanol solution. After displacing adsorbed soil, the adsorbed iodine is then removed by transforming it to water soluble ion with aqueous sodium thiosulfate solution. The final drying process takes place under vacuum pressure with heat from an infra red lamp or a modified microwave oven.

The various contaminated, uncontaminated and regenerated test samples were evaluated by dynamic CCl_4 vapor sorption tests. It was discovered that in the presence of volatile organic contaminants the CCl_4 vapor breakthrough could not be detected by the starch-iodide bubblers of the standard test, and so a flame/copper detector was employed[5]. Continuous CCl_4 vapor test refinement throughout the project culminated in development of an automated four-cup Dawson apparatus with FTIR detector.

In Phase II-A carbon fiber fabric samples were used, and evaluations included agent vapor tests. Uncontaminated as well as seven kinds of variously contaminated and iodine-reactivated samples were tested in triplicate by HD and GD vapors. The cumulative breakthrough criteria[5] for both HD and GD were not reached in any of the tests performed on reactivated, contaminated samples; however, below breaklevel penetration was

detected for the reactivated, diesel fuel-contaminated samples. Samples contaminated with diesel fuel and gasoline suffered rapid breakthrough, while more gradual breakthrough was observed in samples contaminated with cigarette smoke, engine exhaust, and simulated human sweat. However, no breakthrough was observed in samples contaminated with detergent and Freon 113.

In Phase II-B the focus returned to reactivation of Type III foam. Accordingly, emphasis was on application of nonagitative cleaning/reactivation methods that would not abrade the impregnated particles of activated carbon. Investigation of nonaqueous solvent systems and ultrasonic solvent excitation without agitation of the fabric itself led to a second reactivation scheme, which gave 100% reactivation for all the contaminants. Phase II-C exploited a simple, unique, organic solvents sequence for the design of a truck-borne field reactivation unit.

A key feature for successful cleaning with an organic solvent is its strong adsorption potential yet complete removal. We found that methylene chloride can be removed from the activated carbon (AC) by methanol, which does not bind as tightly, and is easily removed.

II. ACTIVATED CARBON GARMENT MATERIALS USED IN THE REACTIVATION STUDY

A. Battle Dress Overgarment[1] (BDO)

The two-layer material is nylon/cotton twill quarpel-treated cover fabric over a layer comprised of a 90 mil polyurethane foam laminate to nylon tricot, that has been impregnated with particles of activated carbon by means of acrylic binder. It is not considered to be routinely frequently washable, and is to be discarded after use.

B. Toyobo KNF-L-1500[3]

The material has an activated carbon (Kynol™) fabric laminated between tricot knit and a pile-surfaced knit, both of polyester. The carbon fiber fabric was chosen for quantitative sorption studies, as it is less subject to carbon loss in liquid baths than is impregnated foam; however, the adhesive between layers dissolved in hydrocarbon contaminants or solvents.

Test pieces, approximately 6" by 6", were cut from large rolls of material, either Type III foam and BDO camouflage cover fabric or the Toyobo KNF-L-1500 laminate with a shell of nylon/modacrylic fabric. In Phase I and IIA the shell fabrics were included as the test samples. With shell stitched to carbon fabric at four corners, samples could be used as an integral entity in contamination, washing, reactivation, and testing phases.

III. CONTROLLED CONTAMINATION

Various selected contaminants were separately applied to the test material in a controlled, reproducible manner. In order to assess the true efficacy of the reactivation process, efforts were made to apply each contaminant to the utmost extent, that is, in a manner far more severe than expected in real life to ensure maximum coverage, full penetration and complete saturation of the contaminant.

A. LAUNDRY DETERGENT

Description: Type II nonphosphate detergent[7]
Concentration: 1.25% solution by weight
Reason for testing: because detergent will be used in the wash cycle to help remove ordinary dirt and grime, it is initially treated as a contaminant to examine if its residue can be removed via the present reactivation process
Method of application: vacuum impregnation (immersing the test sample in a detergent solution under 29" Hg vacuum pressure for approximately 5 minutes)

B. SWEAT

Description: simulated human sweat[8]
Concentrations: 300 mg% (mg/100cc) sodium chloride
90 mg% potassium chloride
230 mg% lactic acid
15 mg% urocanic acid
62 mg% urea
19 mg% citrulline
72 mg% serine
37 mg% alanine
156 mg% leucine
balance water
Reason for testing: sweat is expected to penetrate into the active carbon layer
Method of application: vacuum impregnation at 37 °C for 5 minutes

C. CIGARETTE SMOKE

Description: filterless Camel™ brand cigarette
Concentration: expose to fumes from 10 consecutively burning cigarettes in an essentially closed container (shell fabric is temporarily removed for better exposure to the cigarette fumes)
Reason for testing: expected contaminant in battlefield environment
Method of application: vapor absorption in a closed chamber

D. ENGINE EXHAUST

Description: no-lead gasoline engine exhaust
Concentration: exhaust from an idling engine which was periodically raced to high speed
Reason for testing: expected contaminant in battlefield environment
Method of application: fabric samples separated by half-inch corrugated paper spacers were enclosed in a metal chamber. The exhaust fumes were introduced through a Teflon tube extending deep into the muffler of an automobile. The flow of exhaust fumes was maintained by a small pump located at the exit of the chamber. The total exposure time to the fumes was approximately 12 hours with the automobile engine running for 6 hours. The evacuation pump was shut off whenever the engine is switched off. The engine was periodically raced to supply exhaust fumes generated at a higher engine speed.

E. GASOLINE

Description: no-lead gasoline (Mobil™ brand)
Concentration: 100%
Reason for testing: exposure to gasoline fumes or gasoline spills is expected in a battlefield environment
Method of application: direct immersion (due to the low surface tension of gasoline, penetration and total fouling is expected even without vacuum) for 5 minutes.

F. DIESEL FUEL

Description: regular fuel for automobile with diesel engine (Mobil brand)
Concentration: 100%
Reason for testing: exposure to diesel fumes or spills is expected in a battlefield environment
Method of application: direct immersion (vacuum impregnation is not needed) for 5 minutes

G. LIGHT OIL

Description: Light lubricating oil, Mobil SF10A4
Concentration: 100%
Method of application: vacuum impregnation

H. TRANSMISSION FLUID

Description: Mobil ATF 220
Concentration: 100%
Method of Application: vacuum impregnation

I. FREON 113

Description: Freon TF solvent (manufactured by DuPont, same as Freon 113 with a chemical formula $CCl_2F\text{-}CClF_2$)
Concentration: 100%
Reason for testing: Freon 113 is used in Army dry cleaning equipment and is also used for decontaminating garments fouled by live agents. It is of interest to know if the current reactivation process can be applied to remove Freon residues
Method of application: direct immersion (vacuum impregnation is not required due to Freon's low surface tension) for 5 minutes.

Diesel fuel tends to cause the Toyobo carbon fabric to separate and delaminate. Gasoline and Freon 113 also have the same effect although to a lesser degree. Apparently, solvents such as diesel fuel and gasoline are capable of dissolving the thermobonding adhesive used in the manufacture of Toyobo composite carbon fabric.

IV. IODINE DISPLACEMENT PROCEDURE

A. PRINCIPLE

When a vapor molecule hits a solid surface, the perpendicular component of energy is transferred to the lattice while the tangential component keeps the molecule moving until it hits a wall, with further transfer of energy. The molecule remains bound for a time, due to interaction between its orbiting electrons and the oscillating field of the electrons in the solid, which are similarly interacting with fields of the molecule's electrons (van der Waals bond), but it can be ejected by phonon waves along the solid surface. Deep narrow slit-pores in activated carbon fill with condensed liquid at low partial pressures. Polanyi equated adsorption energy to the work of compressing the vapor to saturation[9]

$$-\Delta F = RT\ln\frac{P_{sat}}{P}$$

Adsorption of large neutral molecules from a solution is similarly proportional to the energy required to concentrate solute molecules to the point of phase separation from the solvent

$$-\Delta F = RTln\frac{C_s}{C}$$

As for sorption of vapors, so also for solutes in poor solvents, migration along the surface of the solid is faster than desorption; adsorption from solution is fast, with stirring, and the large surface available in micropores of activated carbon is filled at low solute concentration. The fractional filling of the available volume by a vapor challenge has a Gaussian dependence[10] on the Polanyi potential (Dubinin):

$$W = W_o e^{-\left(\frac{kL}{\beta} RTln\frac{P_{sat}}{P}\right)^2}$$

L is the width of slit-shaped pores between graphite walls. β is a sorbability coefficient, given by the size and polarizability of the adsorbate molecule, or the nonpolar component of surface tension.

Sorption depends inversely on the width, L, of the activated carbon pore slits. Sorption also depends inversely on solubility C_{sat} of the sorbate in the organic/aqueous mixed solvent; but directly on the coefficient β. β is usually referenced to benzene, and can be estimated from molar refraction M/d x $(n^2-1)/(n^2+2)$, in which molar volume is corrected for free space[11] in the liquid. A more direct estimate of bonding energy between sorbate molecules and graphite surface of activated carbon is the surface tension of nonpolar liquids. The free energy of interaction between two components is the combined cohesion energies, or surface tensions,[12a] of the partners: $-\Delta F = 2\,\gamma_S^{1/2}\ \gamma_{AC}^{1/2}$. The surface tension of I_2, 55.7[12b] dynes/cm is higher than for Br_2, 41.5; perchloroethylene, 31.7[12c]; benzene, 28.9; CCl_4, 26.8; dodecane, 25.4; hexane, 18.4; and Cl_2,

β is larger for molecules with a large number of electrons, such as both halogens and large hydrocarbons. However, Traube's rule of increased sorption with increasing hydrocarbon chain length eventually reverses.[13.] In agreement with a limit are data[12c] indicating that surface tension increases very little with n after n=11. On the other hand, solubility in alcohol ceases after n=13, and this C_{sat} lowering favors oil and fat adsorption. For displacement sorption, we rely on a much larger iodine concentration than is possible for desorbing hydrocarbon.

B. AQUEOUS DISPLACEMENT SOLUTIONS

1. Application solution

Iodine is a stronger displacing agent for activated carbon than most physically bonded adsorbates[3]. It can effectively dislodge and desorb the following:

hydrocarbons	ketones	alcohols
ethers	halohydrocarbons	aldehydes
nicotine	carboxylic acids	carbon disulfide
phenols	organic nitro compounds	DDT
camphor	aromatic dyes	etc.
naphthalene	chlordane	

Although the exact concentration of the iodine is not critical, it should be sufficient for the flow of dissolved iodine passing through the activated carbon to fully desorb the contaminants. In pure water a saturated solution contains only 0.34 g of iodine per liter at 25°C. Addition of solubilizing salts and organic solvent increases iodine solubility[3].

Since an adsorbate can be displaced only into a solvent in which it is soluble, it is desirable to employ the iodine in solution with an organic solvent such as alcohols, xylenes, benzene, toluene, hexanes, halohydrocarbons, etc. In this study iodine dissolved in a 30/70 mixture of water and isopropyl alcohol appeared to be effective as a displacing agent for activated carbon.

In a worst-case scenario, the garment is soiled, stained, covered with grease, contaminated by sweat, exhaust fumes, solvents and hydrocarbons. As a first step, the dirt, stain, some grease and most water soluble contaminants are removed by laundering the garment with detergent in a modified washing machine. After thorough rinsing, an iodine/water/isopropanol solution is introduced. The addition of isopropanol to the aqueous. Being a relatively small molecule and a strong displacing agent for carbon, iodine attaches to the carbon surface, and usurps held adsorbates.

2. Solutions that can release adsorbed iodine

After the displacement treatment, the iodine adsorbed on the carbon surface can be removed by washing in a dilute reducing solution containing one of the following reducing agents:

potassium or sodium sulfite
sulfurous acid
stannous chloride
potassium or sodium thiosulfate
titanium trichloride

The inexpensive sodium thiosulfate, in a dilute solution, was found to be effective and fast-acting. The sodium iodide formed is highly soluble in water and can be washed away easily. The carbon surface is now clean, devoid of contaminants, adsorbates as well as iodine molecules.

C. DRYING METHODS

The wet garment can be spun dry in a conventional washing machine. Instead of using a hot air dryer, the remaining water is removed by vacuum evaporation. Under "mild" vacuum pressure as can be implemented with an inexpensive mechanical pump, the boiling point of water can be lowered drastically, and at room temperature rapid evaporation will occur. Furthermore, volatile contaminants or solvents which may remain can also be boiled away in the same fashion. The heat of evaporation can be replenished via a built-in electric heater or an external infrared heat lamp.

Instead of using a heater or a heat lamp which imparts the thermal energy through the surface of the garment, microwave energy obtainable from an inexpensive commercial microwave oven was also used for vacuum drying. Because a piece of dry material placed in a microwave oven does not absorb microwave energy, the heating process is self-terminating and the thermal energy is imparted directly to all water molecules existing throughout the entire garment.

D. HIGHLIGHTS OF THE PROPOSED METHOD

A list of highlights follows:

(1) Use of iodine, the strongest displacing agent, for desorption of a broad spectrum of contaminants. Iodine has a small molecular size and can readily penetrate deep micropores of the active carbon.

(2) Use of aqueous and organic solvents (for example, 30% water and 70% isopropanol) into which all potential contaminants are soluble.

(3) Use of isopropanol which effectively lowers the surface tension at mesopores and allows access to micropores within the active carbon.

(4) Use of vacuum evaporation for enhancement of vapor phase desorption of volatile contaminants.

(5) Use of microwave-heating of bound water.

In addition, the displacement method requires only minimal power to run a washing machine, a low capacity vacuum pump and an inexpensive, energy efficient microwave oven for drying. The iodine used in the process can be reclaimed with minimal energy expenditure.

E. THE COMPLETE AQUEOUS IODINE-DISPLACEMENT REACTIVATION PROCESS: LAUNDERING; 30% AQUEOUS IODINE REACTIVATION; DRYING

1. The steps of the procedure

The complete steps of the reactivation process for soiled samples are briefly listed and then are described in the sections below:

(1) immerse in water and apply vacuum pressure to remove air in contaminated carbon fabric,

(2) launder in 1.25% Type II nonphosphate detergent at 90°F,

(3) rinse in 90°F water,

(4) transfer laundered sample piece into a 0.1N iodine/water/isopropanol solution at 90°F,

(5) rinse in water,

(6) transfer sample piece into a 90°F 0.1N solution of sodium thiosulfate,

(7) rinse in 90°F water,

(8) squeeze out excess water through rollers and dry the fabric at mild vacuum,

(9) replenish heat of evaporation via an infra-red lamp, or a microwave oven.

2. Detergent wash

The purpose of the initial aqueous laundering cycle is to remove dirt, oil, grime, and water-soluble contaminants. In the present study, all contaminated fabric samples were laundered for 20 minutes in a 90 °F solution containing approximately 1.25% Type II, controlled sudsing, nonphosphate detergent[7]. The sample swirled at the bottom of a tall jar in which the liquid was stirred by a propellar. Earlier test results showed that solutions containing less detergent, such as 0.125%, are not effective in removing oily deposits. Prior to the detergent wash cycle, various contaminant-soaked samples were pre-rinsed in tap water to remove excess amounts of contaminants. The various samples were again rinsed thoroughly in water immediately following the detergent wash cycle.

The water temperature for the detergent wash cycle was approximately 90 °F. This temperature was used although it is inadequate to remove some sweat residue, such as leucine, and the yellow stain from cigarette smoke. At 130 °F leucine will dissolve almost instantly, and the yellow stain can easily be removed during the detergent laundering cycle.

It was also found that use of ultrasound can reduce the washing and rinsing time substantially without any harmful effect.

3. Displacement of contaminants

a. Iodine solution

Following the detergent laundering cycle, the contaminated fabric samples were washed in a 0.1 N iodine solution for approximately 20 minutes. The iodine was dissolved in a solution containing 30% water and 70% isopropanol by volume. Approximately 12.7 grams of iodine, mixed with 19.1 grams of potassium iodide as a solubilizing salt, were slowly dissolved in a small amount of water. Additional water and isopropanol were then added to reach the proper proportion.

Since iodine is a strong displacing agent for active carbon, the small molecules readily penetrate the micropores, adsorb on the carbon surface, and dislodge the contaminants originally adsorbed. This adsorbate displacement phenomenon is possible by virtue of the high electrical polarizability of iodine. The displaced contaminants eventually diffuse to the bulk solution and are later removed by rinsing. The use of an aqueous-organic solvent system (water and isopropanol), which is capable of dissolving potential contaminants, is extremely vital because adsorbates (i.e., contaminants) can desorb only into a solvent in which they are soluble. The use of isopropanol also facilitates solvent wetting the edges of, and penetration into, micropores, by lowering the surface tension of water.

b. Iodine removal

After the displacement treatment, the active sites on the carbon surfaces are occupied by adsorbed iodine atoms. The activated carbon will return to its original activity if these iodine atoms can be removed. In the present study, the adsorbed iodine was removed by washing in a dilute reducing solution of sodium thiosulfate. This reaction can be expressed as follows:

$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$$

The sodium iodide formed is highly soluble in water and it does not adsorb on the carbon surface. Sodium thiosulfate solution at a concentration range of 0.01 N to 0.1 N was found to be effective for complete removal of adsorbed iodine, and can be rinsed away with water.

4. Vacuum drying with infrared heat

After rinsing away the NaI, $Na_2S_4O_6$ and excess amount of unreacted $Na_2S_2O_3$, the carbon surface is clean. The drying process takes place under low pressure with heat supplied by an infrared heat lamp controlled by a variac transformer.

5. Vacuum drying in a microwave oven

When during vacuum drying the heat was supplied by a microwave oven, Type III foam gave enhanced sorption values in all three types of CCl_4 sorption tests (*vide infra*): Phase I test results have shown that some reactivated active carbon material exhibited a far better CCl_4 adsorption capacity than that of a fresh sample

(Table 4). Also, it was demonstrated in repeated experiments that uncontaminated Type III foam, subjected to wetting and subsequent vacuum drying in the presence of microwaves, can achieve up to 40% increase in CCl_4 adsorption capacity. This effect was at first believed to be due to additional activation of the carbon surfaces by microwave-excited water molecules. Vacuum drying with an infrared lamp does not show any noticeable enhancement in the CCl_4 adsorptive activity.

The effect of microwave heating studied in later phases of the project showed that it is moisture alone that enhances sorptivity of impregnated foam, rather than a microwave-induced activation of carbon. Industrial processes used for production of active carbons generally consist of carbonization of the source material and activation with steam at elevated temperature (1600 - 2000°F). In drying the fabric in a microwave oven, evaporated water molecules are not excited at the microwave frequencies of the oven (kHz).

Charged particles, if they are present, can be accelerated by the microwave field; however, no enhancement of sorptivity was detected for the activated carbon fiber fabric, Toyobo KLF-1500, after microwave drying. Further, Type III foam was studied at Natick, and found to routinely show 15-20% enhancement after immersion in water, and air-drying. There is potential for additional sorption by the latex-impregnated activated carbon particles, since the sorptivity is always lower than for the same weight of pure carbon particles.

The water-induced enhancement of sorptivity of the impregnated carbon in Type III foam is therefore thought to be the basis of the microwave effect and is caused by swelling of the latex binder. The impregnate composition is 20 polymer:80 AC. The effect of water on solid polymer containing hydrophylic groups is to restructure slowly the surface[14]. The observed increase in sorption is then due to polymer moving away from pore openings, or to sorption by exposed nonpolar segments of the polymer, which coalesce if they are dry.

A commercially available microwave oven was used in the present investigation. A laboratory test system suitable for the microwave enhancement study is schematically shown in Figure 1. It consists of a commercial microwave oven, a vacuum drying chamber, a pump, a pressure transducer, and a viewing port. A steam generator and a servo-valve system were also incorporated for precise control of the chamber pressure. This test system was designed to determine the optimum steam pressure and microwave energy for carbon activation. Some of the relevant specifications of these equipment items are summarized as follows:

Microwave oven

Manufacturer: Amana Refrigeration, Inc. Amana, Iowa
Model: RR - 1110
Frequency: 2450 MHz
Microwave Power: 1000 Watts
Electrical Rating: 110 V and 20 A
Duty Cycle Control: 0 to 100% with a time base of 0.5 second (minimum "ON" time per cycle)

Vacuum pump

Manufacturer: Sargent-Welch Scientific Company, Skokie, Illinois
Model: 1402
Type: 2-stage rotary
Capacity: 160 liter per minute
Dead End Pressure: 1 x 10^{-4} Torr

Vacuum Pressure Transducer

Manufacturer: Datametrics/Dresser Industries, Inc., Wilmington, Massachusetts
Model: 600 Barocel

Vacuum Chamber

Manufacturer: Corning Glassworks, Corning, New York
Size: 6" I.D. x 7.5" O.D.

Material: Pyrex glass end cap. As depicted in Figure 1, the original door of the microwave oven was replaced by a 1/2 inch aluminum plate on which a glass vessel was attached via a metallic clamping ring. Detachable couplers of gas inlet, pump outlet, pressure transducer, pressure gauge, and a quartz viewing window were all connected to the aluminum plate within the open area of the vacuum chamber.

Fine copper screens of a mesh size comparable to that of the original door were installed on various inlet ports to prevent external leakage of microwave energy. In the absence of the original door, the concealed multiple safety interlocks must be by-passed before the microwave oven can be switched on. For the particular door design used in the Amana microwave oven, extra aluminum deflection plates must be installed around the oven to reduce microwave leakage through the gap between the half-inch aluminum plate and the opening of the oven. The maximum leakage through the seams of the oven, the vacuum lines, and the viewing port was found to be well within the safety guideline established by the Federal Government (5 mW/cm^2 at a distance of 5 cm). The leakage energy was measured with a Model HI-1500 microwave survey meter manufacturred by the Holaday Industries, Inc., Eden Prairie, Minnesota. The chamber pressure was measured by means of a capacitance type Barocel pressure transducer. The feedback control circuit bleeds in the proper amount of steam to maintain a desired chamber pressure.

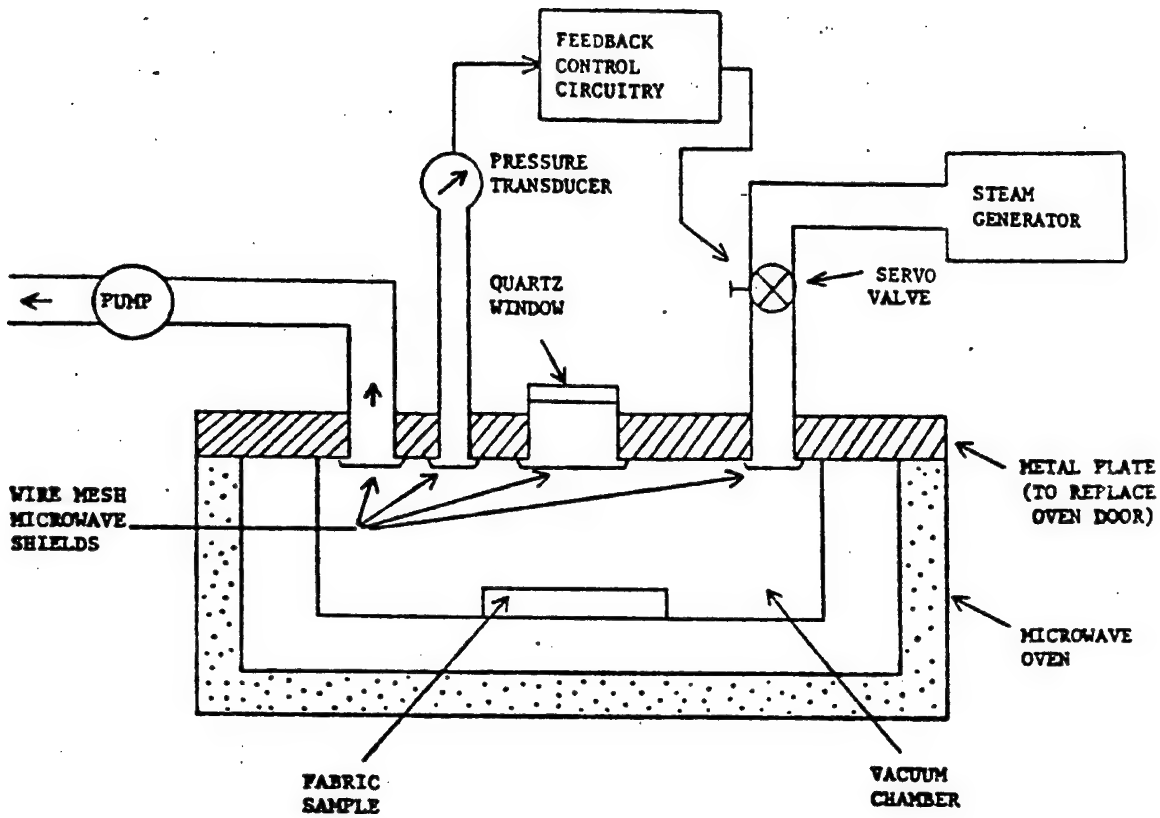


Figure 1. Schematic diagram of a microwave vacuum oven

V. ASSAY TESTS: BREAKTHROUGH OF CHALLENGE VAPOR

The ability of carbon fabric to adsorb chemical agents can be determined directly by means of live agents or indirectly by means of an agent surrogate.

A. CARBON TETRACHLORIDE VAPOR ADSORPTION TESTS

1. Standard Dawson CCl_4 Test

The ability to adsorb chemical agent can be evaluated more readily by using the agent surrogate CCl_4 in the procedure for testing impregnated foam given in MIL-C-43858A GL[1b]. Five mg/liter of carbon tetrachloride in nitrogen at 90 °F, are allowed to pass at a rate of 1 liter/minute through the permeable test fabric, which is mounted in a 100 cm^2 sample cup. When the sample reaches its adsorptive capacity, CCl_4 will penetrate (break through) the fabric and be detected downstream by a pyrolyzer and starch/iodide indicator solution. The amount of CCl_4 adsorbed by the sample is proportional to the time delay (breaktime) of the appearance of carbon tetrachloride, and it can be expressed in weight per unit area. The constant CCl_4 flow rate can be measured before introducing the sample into the flow stream, by flowing it directly into an active carbon-filled Schwartz tube, which is weighed after a fixed collection time.

In the present study, a minor modification of the standard apparatus[1b] was required. It was discovered that an appreciable amount of room air can be drawn into the Dawson cup through the rims where metal and test specimen were compressed together. This leakage was especially serious for a Toyobo material studied in Phase IIA, because of its piled surface, thickness, and fiber-knit construction. Despite the clamping action provided by a large steel "C" clamp, a significant amount of air could still be drawn into the sample cup by the vacuum pump located downstream.

Air leakage was prevented through installation of three butyl gaskets. An inner gasket, having an outside diameter of 5.5" and an inside diameter of 5", is sandwiched between two identical outer gaskets having the same outside diameter but a smaller inside diameter of 4". The diameter of the test specimen was reduced from 5.5" to 5" in order to butt against the inside of the inner gasket. The thickness of the inner gasket (30 mil) was chosen to approximate the thickness of the test specimen under compression. By overlapping the inner gasket and part of the test specimen, the outer gaskets provide a good seal at the rims of the Dawson cup as well as at the outer edges of the test specimen. Results of repeated tests indicated that air leakage has been eliminated.

Detection of CCl_4 penetration in the standard test of MIL-C 43858 is through pyrolysis and blue coloration in starch-iodide bubblers. For Phase I feasibility studies in IBS laboratories the more portable apparatus with copper-halide flame detection that is approved for quality control[5] was employed.

In Phase IIA, all standard CCl_4 dynamic adsorption tests were conducted at US Army Natick Research, Development & Engineering Center using on-site facilities. It was discovered that in the presence of certain organic contaminants, the standard dynamic CCl_4 vapor penetration test, with detection by starch-iodide bubblers, gave erroneous results. The breaktime and adsorption data for Toyobo active carbon fabric samples contaminated with cigarette smoke, engine exhaust, gasoline, and diesel fuel, respectively, are summarized in Table 1.

Table 1. Dynamic CCl_4 tests with starch-iodide bubblers: adsorption data for samples fouled by hydrocarbon contaminants (Toyobo activated carbon fiber fabric)

Sample Description	Test Station	Average CCl_4 Flow (mg/min)	Breaktime (min)	CCl_4 Adsorption (mg/cm^2)
Uncontaminated control	1	6.0	48	2.9
Cigarette smoke-contaminated	2	5.7	> 86	> 4.9
Cigarette smoke-contaminated	3	5.7	> 86	> 4.9
Cigarette smoke-contaminated	4	5.7	> 86	> 4.9
Uncontaminated control	1	5.4	53	2.9
Engine exhaust-contaminated	2	5.0	104	5.2
Engine exhaust-contaminated	3	5.0	60	3.0
Engine exhaust-contaminated	4	5.8	75	4.4
Uncontaminated control	1	6.0	52	3.1
Gasoline-contaminated	2	5.7	> 153	> 8.7
Gasoline-contaminated	3	5.7	> 153	> 8.7
Gasoline-contaminated	4	5.7	> 153	> 8.7
Uncontaminated control	1	6.4	51	3.3
Diesel fuel-contaminated	2	5.8	> 185	>10.7
Diesel fuel-contaminated	3	5.8	> 185	>10.7
Diesel fuel-contaminated	4	5.7	> 185	>10.6

According to the data given in Table 1, all contaminated samples yielded far better CCl_4 adsorption than the uncontaminated control samples. This anomaly can be attributed to the existence of hydrocarbons which interfere with the detection of CCl_4 penetration when the pyrolyzer/starch-iodide bubbler system is used; that is, the iodine-amylose complex is not formed[15,16]. Therefore, in the presence of hydrocarbon contaminants, another detection system is used to detect CCl_4 penetration.

2. Simplified carbon tetrachloride adsorption test

The more portable copper/flame detector CCl_4 adsorption test was used initially in Phase I, and when hydrocarbon interference with the bubbler indicator solution (iodide / starch solution) was discovered, it was of necessity also used in later work, for samples that had been exposed to hydrocarbons. This is the simplified CCl_4 adsorption test devised by Defense Personnel Support Center (DPSC) for contractors' use in quality control, and evaluated by Natick Labs[5]: It uses a copper-flame halide detector to measure the penetration of CCl_4 vapor (Figure 2).

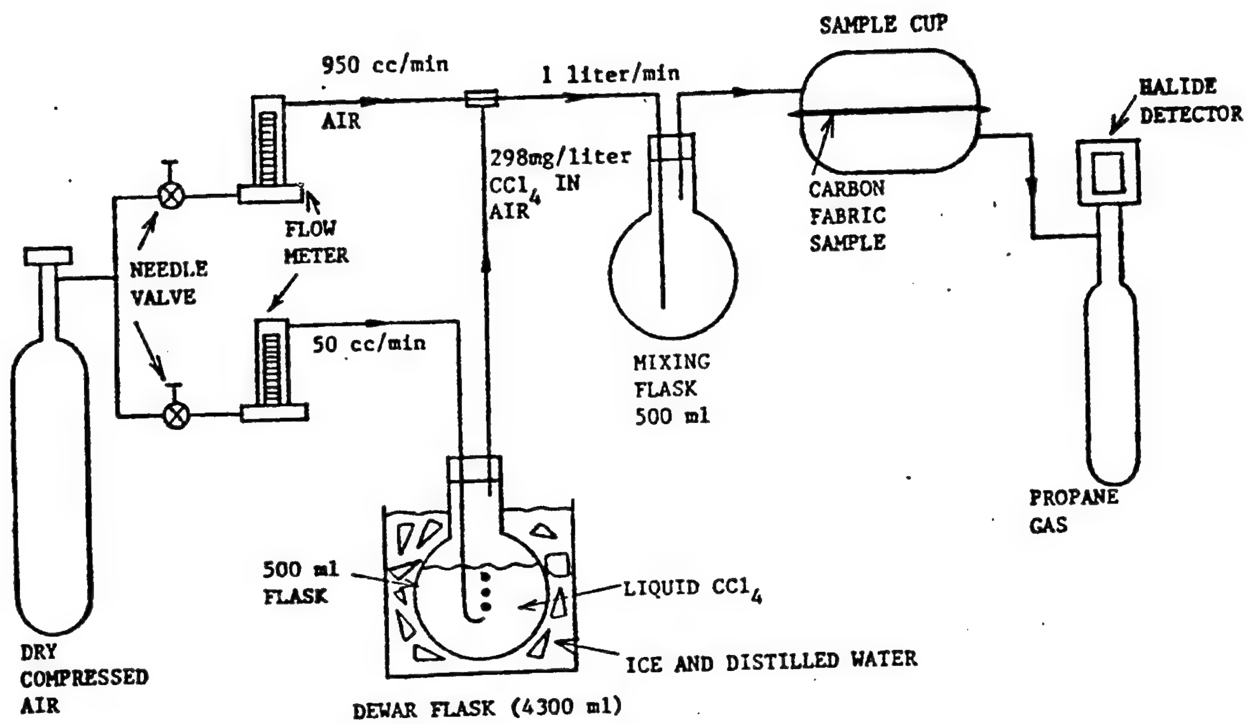


Figure 2. Simplified CCl_4 adsorption apparatus for specimens containing hydrocarbon contaminants

A stream of dry air maintained at 50 cc/min is bubbled through a CCl_4 solution at 0°C. The resulting stream becomes saturated with CCl_4 vapor. The partial pressure of CCl_4 is given by the following equation[17]

$$\log_{10}P = 8.004 - 0.05223x\frac{33914}{T}$$

where P is the partial pressure in mm Hg and T is the absolute temperature in K. At 0°C, the CCl_4 partial pressure is calculated to be 33 mm Hg, whereas the CCl_4 density is approximately 298 mg/liter. As shown in Figure 2, this air stream, which is saturated with CCl_4, is then diluted with another dry air stream maintained at 950 cc/min. The total air flow is 1 liter/min, and the CCl_4 flow is approximately 14.9 mg/min. The actual CCl_4 flow rate can be verified with a Schwartz tube filled with activated carbon.

Initially, the carbon tetrachloride is completely adsorbed by the test specimen and the flame is blue at the propane/copper halide detector. As the test sample becomes saturated CCl_4 will pass through and the flame color of the detector will change to green. The elapsed time from the instant the sample cup is engaged to the moment when a green flame is first observed is recorded as the initial breaktime. When the CCl_4 starts to penetrate at a higher rate so that a large green flame appears, completely filling the space above the copper reaction plate, the elapsed time at this end point is also recorded as the final breaktime. Control samples were always run as one of the four samples in the four-cup test apparatus.

3. Static carbon tetrachloride adsorption test

The static test described here is intended for the determination of the total carbon tetrachloride adsorption capacity. It is devised solely for speedy evaluation and quality control purposes. An air stream containing 14.9 mg/liter of CCl_4 is allowed to pass through the fabric sample maintained at room temperature, until there is no further increase in the weight of the fabric. The percentage increase in the weight of the carbon fabric is the measure of carbon tetrachloride adsorption activity. Since this is a test to equilibrium, the carbon tetrachloride activity as defined here does vary slightly with the concentration of CCl_4 in the air stream. The apparatus used for the static test is identical to that of Figure 2 with the deletion of the propane halide detector. Weighed 2" by 2" samples are placed inside the Dawson cup, which is then sealed. Advantages of the static adsorption test are:

(1) it yields more reproducible results,
(2) it is efficient and less time consuming,
(3) it is less sensitive to the flow rate of CCl_4,
(4) it is not sensitive to the presence of pinholes, surface nonuniformity, and loss of carbon due to handling and washing,
(5) it allows simultaneous testing of multiple samples,
(6) there is no problem associated with sealing and leakage between the fabric and the rims of the Dawson cup.

B. LIVE AGENT TESTS

Live agent testing was conducted at Battelle Columbus Laboratories, West Jefferson, Ohio. Mustard (HD) and soman (GD) in vapor phase were used as the challenging agents. The performance of various fresh, contaminated and reactivated carbon fabric samples was evaluated using the standard vapor challenge/vapor

penetration permeation test procedures[6]. A summary of the experimental conditions are presented in Table 2 below:

Table 2. Experimental conditions for live agent test

Agent	Vapor Concentration (µg/liter)	Challenge Air Flow Rate (liter/min)	Challenge Air Humidity (% RH)	Test Temperature (°F)	Duration (hour)
HD	20 ± 2	1.0	80 ± 2	90 ± 2	150
GD	10 ± 1	1.0	80 ± 2	90 ± 2	150

The effluent stream of each test cup was sampled every 24 hours until penetrating agent was detected; then samples were taken alternately after 8 and 16 hours until the end of the test (150 hours) or until breakthrough. Breakthrough criteria are 4 µg HD/cm^2 and 10 µg GD/cm^2.

Vapor sampling was performed using sorption bubblers filled with 20 mL of ethylene glycol diacetate (EGDA). The contents of these bubblers were removed after the required sampling interval and analyzed directly by gas chromatography using a Hall detector (GC/Hall). These analytical data were then used to calculate the amount of agent permeation through the exposed area of each sample, i.e. µg of penetrated agent per cm^2 of sample.

The challenge vapor stream was sampled periodically each day of the test to determine the vapor concentration in the challenge stream. Samples were collected using sorption bubblers and analyzed by GC as described above. These data were used to (1) calculate the average vapor challenge concentration as a function of time and (2) adjust the operation of the vapor generator as required to maintain the vapor challenge at the specified value. The average daily challenge concentration was then used to adjust the observed breaktimes to the specified challenge.

Because of the importance of defining and maintaining the vapor challenge concentration, sampling and analysis procedures were employed that were somewhat more rigorous than those recommended in CRDC-SP-84010[6]. These documents suggest that 15 liters of the challenge vapor stream be sampled twice daily, between 0800 and 1600 hours. However, in order to preclude the possibility of undetected fluctuations in the challenge vapor concentration and in an effort to maintain strict control over this parameter, a sampling approach was employed in the present study in which the vapor challenge was monitored more frequently. Also samples were drawn from two different locations in the challenge manifold. The 15-liter samples were drawn at the beginning, middle and end of the workday (i.e. nominally 0800, 1200, and 1600 hours). Also, 5-liter samples were obtained approximately once every two hours between 0800 and 1600 hours. Sampling was performed using liquid-filled sorption bubblers as described above and a sampling flowrate of 1 L/min. The 15-liter samples were drawn from a downstream port in the manifold, while the 5-liter samples were obtained at an upstream location.

Gas chromatographic analysis was used to assay the HD or GD in the bubbler samples obtained in these tests. The analytical detection limit was at least 0.1 µg HD/mL and 0.125 µg GD/mL during each set of

analyzed. This detection limit is estimated based on the concurrent analysis of standard samples prepared at or below these levels and analyzed at the same time. The estimated permeation detection limits for the penetration for each sample are 0.02 μg HD/cm^2 and 0.026 μg GD/cm^2. For a test requiring seven bubblers, the cumulative GD penetration data obtained in these evaluations may be in error by as much as 0.18 μg GD/cm^2. Similarly, the HD data may be in error by as much as 0.14 μg HD/cm^2. Although relatively small compared to the breakthrough levels for any of the samples evaluated in this study, these error limits should be taken into consideration when interpreting these data.

Data calculation methods are summarized as follows. Values for Cumulative Lapsed Time, Penetration, and Cumulative Penetration were calculated for each material sample from the Bubbler Concentration and Lapsed Time values generated. These calculated data were then used to determine the Breaktime and Adjusted Breaktime for each sample. Similarly, the cumulative average vapor challenge concentration was calculated as a function of time from the individual concentration bubbler samples. These data were separately averaged for each day to give daily average agent concentration values, which were then averaged in a cumulative manner to give average agent concentration of the challenge.

VI. RESULTS ON I_2 DISPLACEMENT OF SOILS IN AQUEOUS MIXED SOLVENT

A. PHASE I: FEASIBILITY STUDY ON THE BDO AC/FOAM AND COVER

1. Soils

Detergent, sweat, cigarette smoke, engine exhaust, light lubricating oil, dirt, transmission fluid, and a 1:1 mixture of gasoline and diesel fuel were applied to 5-1/2" diameter samples of Type III foam and camouflage twill cover fabric, as described in Section III.

2. Cleaning and reactivation

The cleaning and reactivation routine (with no microwave oven drying), Section IV E, was followed. In the vacuum drying step, only an infrared heat lamp was used for the soiled and reactivated samples.

3. Simplified CCl_4 vapor adsorption tests

To determine the feasibility of the iodine displacement reactivation process, tests were performed at IBS using the more portable apparatus of the simplified test, with detection by the green color produced by CCl_4 in a flame from a propane torch with copper collar. Though less sensitive than the starch-iodide bubbler color change, the simplified method escaped the error caused by interference of hydrocarbon contaminants with iodine-starch complexation. Results are shown in Table 3 for tests to breakthrough (3A) and equilibrium (3B).

Table 3. Adsorption Tests on Contaminated and I_2 Displacement - Reactivated AC/foam Samples

Table 3A. *Simplified Dynamic CCl_4 Tests (Copper-flame)*

Contaminant	Treatment	CCl_4 Adsorption (mg/cm^2)	Average (mg/cm^2)
None	None	2.45	
		2.08	
		2.15	2.23
None	Vacuum Evacuation	2.61	
		2.44	
		2.56	2.54
Detergent	Water Rinse	2.74	
	Vacuum Evacuation	2.31	
		2.48	2.51
Sweat	Vacuum Evacuation	2.07	
		1.81	
		1.72	1.87
Sweat	Iodine/Water/Isopropanol	2.70	
		2.56	
		2.33	2.53
Cigarette	None	1.86	
Smoke		1.54	
		1.08	1.49
Cigarette	Iodine/Water/Isopropanol	2.60	
Smoke	Vacuum Evacuation	2.23	
		2.28	2.37
Engine	None	2.20	
Exhaust		1.88	
		1.64	1.91
Engine	Iodine/Water/Isopropanol	2.77	
Exhaust	Vacuum Evacuation	2.39	2.58
Petroleum Products	None	Not Tested	
Petroleum	Iodine/Water/Isopropanol	2.68	
Products	Vacuum Evacuation	2.08	2.38
Oil	None	Not Tested	
Oil	Iodine/Water/Isopropanol	2.08	
	Vacuum Evacuation	1.78	
		1.88	1.91 *(Con'd)*

Table 3A. *Simplified Dynamic CCl_4 Tests (Copper-flame) (Con'd)*

Contaminant	Treatment	CCl_4 Adsorption (mg/cm^2)	Average (mg/cm^2)
Oil	Perchloroethylene Vacuum Evacuation	2.14 2.08	2.11
Dirt	None	2.02	2.02
Dirt	Iodine/Water/Isopropanol Vacuum Evacuation	2.78 2.43 2.20	2.47
Trans-mission Fluid	None	Not Tested	
Trans-mission Fluid	Iodine/Water/Isopropanol Vacuum Evacuation	2.14 1.99	2.06
Trans-mission Fluid	Perchloroethylene; Vacuum Evacuation	2.23	2.23

Table 3B. *Equilibrium Adsorption Tests*

Contaminant	Treatment	CCl_4 Adsorption,% of sample weight	Std Deviation	Max./Min.
None	None	12.3	1.5	14.6/9.54
None	Vacuum	14.5	1.6	17.0/12.4
Detergent	Vacuum	14.2	1.4	16.2/12.1
Sweat	Vacuum	9.6	1.2	11.2/8.2
Sweat	I_2/Water/i-propanol; Vacuum	14.8	1.4	16.5/12.9
Cigarette Smoke	None	8.4	1.0	9.5/7.2
Cigarette Smoke	I_2/Water/i-propanol;Vacuum	14.1	1.5	16.1/11.8
Engine Exhaust	None	9.0	1.9	11.2/6.0
Engine Exhaust	I_2/Water/i-propanol;Vacuum	15.8	1.5	17.4/13.8
Petroleum Products	I_2/Water/i-propanol; Vacuum	13.6	0.6	14.1/12.4
Oil	I_2/Water/i-propanol; Vacuum	10.2	2.1	13.2/6.5
Oil	Perchloroethylene; Vacuum	11.8	0.5	12.4/11.2
Dirt	I_2/Water/i-propanol; Vacuum	15.5	1.9	18.4/13.2
Transmission Fluid	I_2/Water/i-propanol; Vacuum	11.5	1.1	12.3/9.6
Transmission Fluid	Perchloroethylene; Vacuum	14.6	0.9	16.1/13.8

4. Vacuum drying in a microwave oven

In Table 4, dynamic CCl_4 (Cu-flame detector) tests compare the results obtained with microwave/vacuum oven and infrared/vacuum oven drying of uncontaminated samples that were wetted and dried with vacuum and either infra-red or microwave heat. Additional "static" equilibrium tests similarly compare the effect of the methods for reactivated smoke- or exhaust-contaminated, samples.

Table 4. The Effect of microwave heating during vacuum-drying of ac-impregnated foam

Dynamic tests on untreated samples; static tests on samples contaminated and reactivated with iodine in aqueous isopropanol.

❖ *Simplified dynamic CCl_4 vapor breakthrough adsorption tests*

Treatment	CCl_4 Adsorption at breakthrough (mg/sq cm)	Average	Ratio
Wetted, vacuum, IR heat	2.61		
Wetted, vacuum, IR heat	2.44		
Wetted, vacuum, IR heat	2.56	2.54	= 1.00
Wetted, vacuum, microwave	3.69		
Wetted, vacuum, microwave	3.40		
Wetted, vacuum, microwave	3.36	3.48	1.37

❖ *Equilibrium (static) adsorption tests (per cent weight increase)*

Contaminant - Treatment	CCl_4 Adsorption at equilibrium (% weight increase)	Standard Deviation	Ratio
None - Wetted, vacuum, IR heat	14.5	1.6	= 1.00
None - Wetted, vacuum, microwave	22.2	0.6	1.53
Cigarette smoke - I_2, Wetted,vacuum, IR heat	14.1	1.5	.97
Cigarette smoke - I_2, Wetted, vacuum, microwave	18.5	0.6	1.27
Exhaust fumes - I_2, Wetted, vacuum, IR heat	15.8	1.5	1.09
Exhaust fumes - I_2, Wetted, vacuum, microwave	21.8	1.0	1.50

5. Conclusions regarding feasibility

The samples tested in Table 3 were dried with infrared, vacuum oven. Results show that the activity of samples saturated with lighter soils, causing 25 to 40% inactivation (sweat, exhaust, smoke), is completely restored by the iodine displacement process, while fuel and oil-soaked samples are 75 to 94% restored. Oil soaked samples were also incompletely reactivated by perchloroethylene. Super activation is possible if microwave drying is used, Table 4. Loss of carbon particles was evident, but was not accompanied by loss of activity.

The primary goal of developing a reactivation process for chemical protective garments appears to be achievable. Although only Type III AC-impregnated foam was studied, the same process is expected to be applicable to carbon fibers or any other active-carbon-based material. Iodine staining of the shell fabric of the garment is not a problem, and no color change nor degradation of water repellency was observed.

B. PHASE IIA: QUANTITATIVE STUDY

Activated carbon fiber fabric samples do not spontaneously deposit carbon into solvent, and should provide reliable quantitative estimates of reactivation. The activated carbon fabric system manufactured by Toyobo Company, Japan, was chosen as a test substrate for contamination and reactivation. The fabric system, designated as KNF-L-1500 has an ACF knit made from pyrolyzed and activated phenolic fiber (Kynol), laminated between polyester tricot and a knit with a pile surface, which is fluorocarbon coated.

Soils application and reactivation were performed in a controlled, reproducible manner (Controlled contamination, section III; Activation, section IV E). Soils were applied to the utmost extent, far more severe than expected in real life, to ensure maximum coverage and complete saturation of the contaminant. Laundry detergent and Freon 113, as well as cigarette smoke, engine exhaust, sweat, and gasoline and diesel fuel, both as fumes and as liquid were studied. The microwave vacuum oven was used routinely for drying all fully reactivated samples.

Assay of reactivation was done by testing sorptive capacity before and after contamination, and after steps in the reactivation process were applied to contaminated samples. Live agent testing was conducted at Battelle Columbus Laboratories, and CCl_4 testing was performed in a simplified (copper-flame detection) apparatus at IBS.

1. GD vapor tests

Seven triplicates of fully reactivated samples and uncontaminated triplicate samples were challenged with GD vapor for 150 hours. The test samples within each group had been identically contaminated and reactivated under the same conditions, based on the experimental methods presented in Sections III and IV. A summary of the cumulative penetration at the time the test was ended is provided in Table 5. Throughout the entire 150 hour test period, breaklevel penetration was not observed in any of the GD tests performed in this study. The data in Table 5 present only the cumulative penetration at the end of the test period.

The 24 labeled samples for GD evaluations were performed by Battelle in conjunction with identical tests being performed under another Battelle contract. Because only a limited number of test stations were available, these GD evaluations were not all performed simultaneously, but instead were performed in groups of 5, 12, or 2 samples at a time.

Table 5. GD penetration test results: Toyobo samples; different contaminant groups

IBS Sample Code	Battelle Sample Number	Contaminant Group	Reactivation Process*	150-Hour Cumulative Penetration (µg/cm2)
B12L	9G	None (control)	None	BDL**
L22A	13G	None (control)	None	0.06
A32B	17G	None (control)	None	BDL
			AVG.= 0.02	
G11A	1G	Gasoline	L,I,M	BDL
A23S	10G	Gasoline	L,I,M	BDL
S32G	14G	Gasoline	L,I,M	BDL
			AVG. = 0.	
X23H	2G	Engine Exhaust	L,I,M	BDL
E14X	15G	Engine Exhaust	L,I,M	BDL
H35E	20G	Engine Exhaust	L,I,M	0.49
			AVG.= 0.16	
E31D	3G	Diesel Fuel	L,I,M	0.17
I27E	11G	Diesel Fuel	L,I,M	0.26
D12E	21G	Diesel Fuel	L,I,M	0.09
			AVG.= 0.17	
S130	24G	Cigarette Smoke	L,I,M	BDL
M210	4G	Cigarette Smoke	L,I,M	0.06
033M	23G	Cigarette Smoke	L,I,M	BDL
			AVG.= 0.02	
W24E	6G	Simulated Sweat	L,I,M	0.12
E34S	18G	Simulated Sweat	L,I,M	0.12
S12W	19G	Simulated Sweat	L,I,M	BDL
			AVG.= 0.08	
O11A	5G	Detergent	L,I,M	BDL
A22P	12G	Detergent	L,I,M	0.15
P31S	22G	Detergent	L,I,M	BDL
			AVG.= 0.05	
O31F	7G	Freon 113	L,I,M	2.98
E23O	8G	Freon 113	L,I,M	2.14
F14E	16G	Freon 113	L,I,M	0.79
			AVG.= 1.97	

* Reactivation process identification

L - laundering with detergent

I - iodine treatment

M - microwave activation

** BDL - Below detection level

Over the 150-hour test period, none of the reactivated samples reached the cumulative breakthrough criterion set for GD vapor (10 μg/cm^2).

2. HD vapor tests

The various types of samples undergoing mustard (HD) gas penetration tests included uncontaminated controls, contaminated, partially reactivated, and completely reactivated samples. Among these groups, the partially reactivated samples were tested for the purpose of determining the benefit of

(1) laundering with Type II detergent followed by washing in isopropyl alcohol,

(2) laundering with Type II detergent, washing in isopropyl alcohol, followed by microwave activation.

A summary of cumulative HD penetration for various sample groups are presented in Table 6. The HD evaluations were performed in different batch sizes, ranging from 2 to 22. During the course of these evaluations, in several cases, the challenge and analysis procedures were temporarily suspended. These temporary suspensions were necessitated by power interruptions and other matters, which prevented the continuous operation of the test apparatus. During each temporary interruption in the test, the sample cups were completely isolated from the test apparatus by closing inlet and outlet valves of each cup.

The actual performance of various fabric samples can be visualized in a graphic form with the cumulative HD penetration plotted against the lapsed time. In Figure 3, the time variation of the cumulative penetration of uncontaminated control samples exhibited some divergence and no explanation can be found for the substantial deviation of curve 7 from curves 1 through 6. Graphs of cumulative penetration for contaminated and for fully reactivated samples are presented in Figures 4 through 10.

Observations based on trend graphs and data presented in Table 6 can be summarized as follows:

(1) Over the 150-hour test period, none of the fully reactivated samples (identified by processes L,I,M) reached the standard cumulative breaklevel criterion for HD (4 μg/cm^2).

(2) Breaklevel penetration occurred in all three triplicate samples contaminated with gasoline or diesel fuel, and in one of each of the triplicate samples contaminated with engine exhaust, cigarette smoke, or simulated sweat .

(3) Breakthrough was not observed in samples contaminated with Type II detergent and Freon 113.

(4) Partially processed samples (identified by processes L.S or L.S.M) generally have less adsorptive capacity.

(5) The fully reactivated samples, although not as good as the control in every case, perform nearly equivalently. The present reactivation processes shows promise as a viable method for reactivation of carbon fabrics.

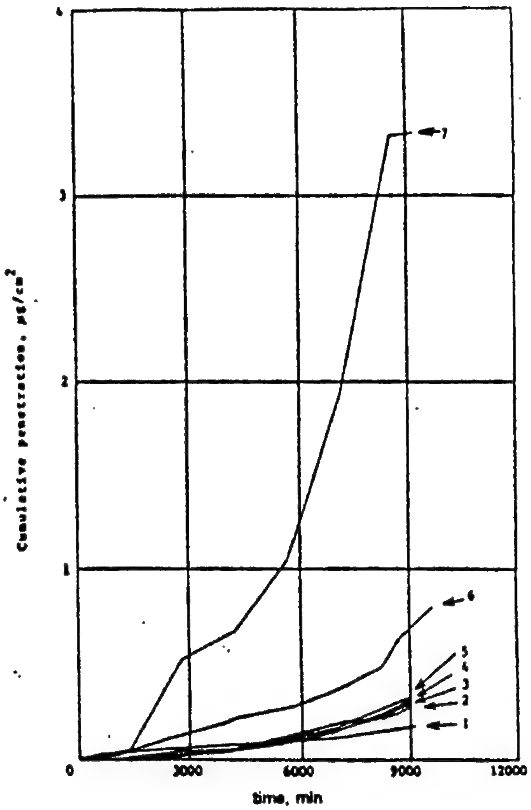


Figure 3. Cumulative HD penetration of seven replicate samples of fresh carbon fabric.

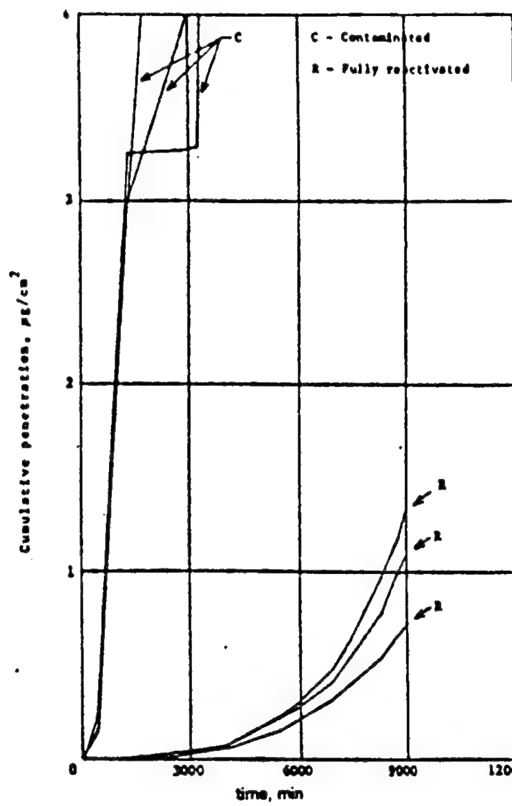


Figure 4. Cumulative HD penetration of gasoline-contaminated and iodine-reactivated carbon fabric

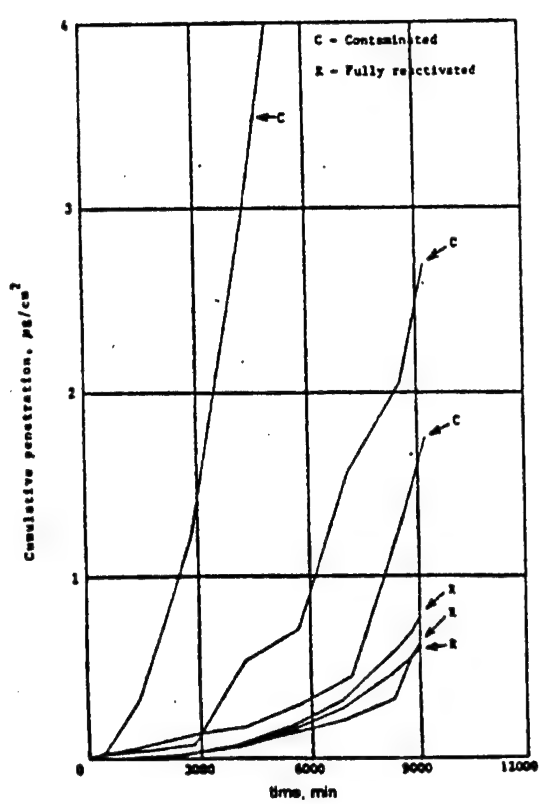


Figure 5. Cumulative HD penetration of engine exhaust-contaminated and iodine-reactivated carbon fabric

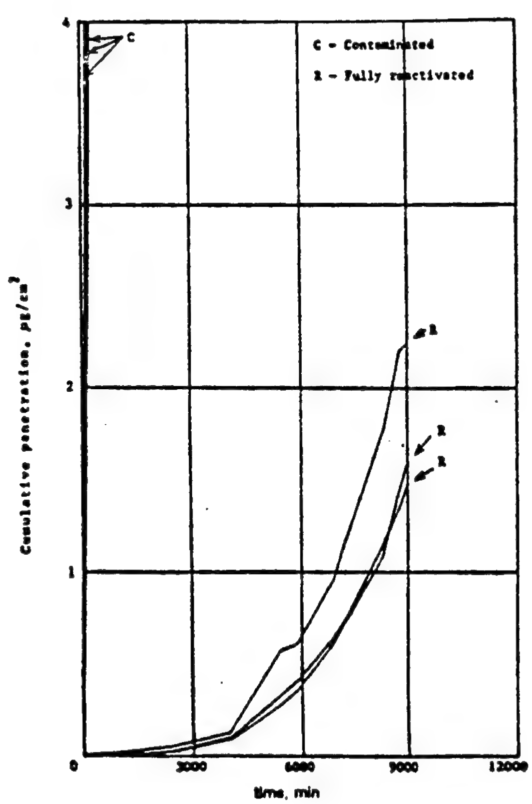


Figure 6. Cumulative HD penetration of diesel fuel-contaminated and iodine-reactivated carbon fabric

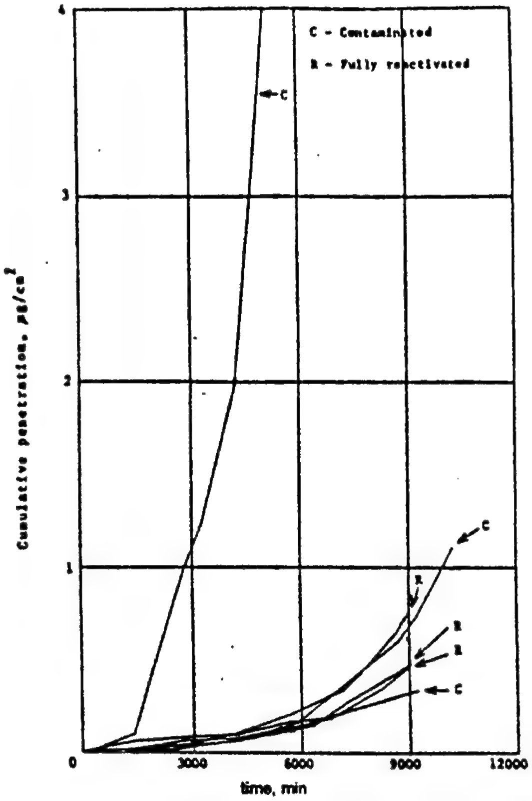


Figure 7. Cumulative HD penetration of cigarette-smoke contaminated and iodine-reactivated carbon fabric

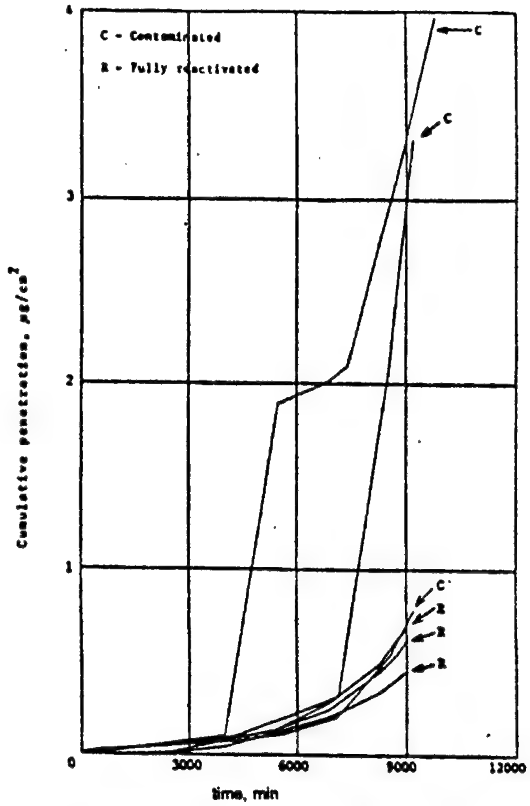
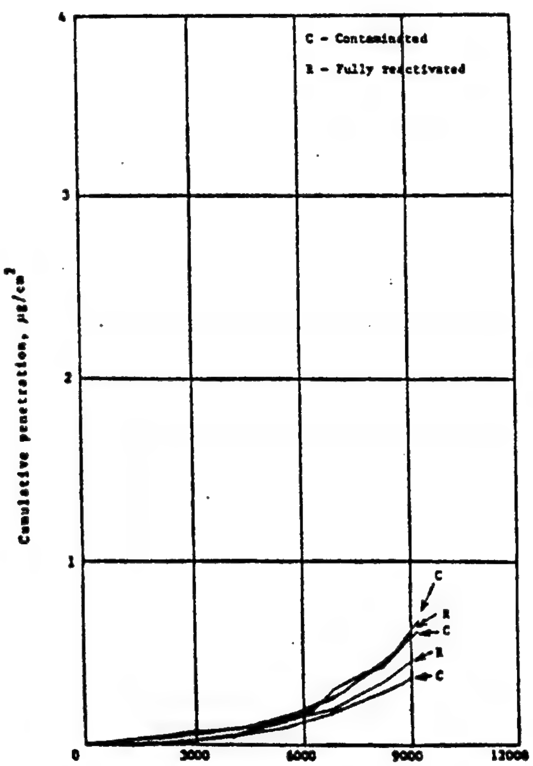
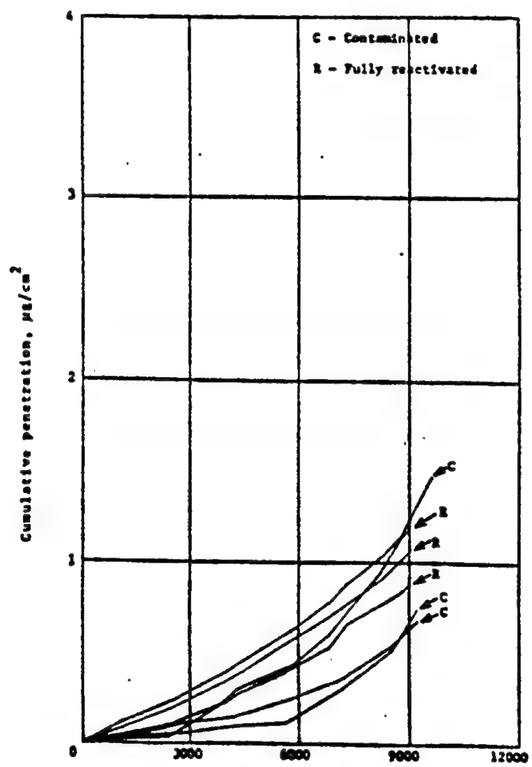


Figure 8 Cumulative HD penetration of simulated human sweat contaminated and iodine-reactivated carbon fabric



time, min

Figure 9. Cumulative HD penetration of detergent-contaminated and iodine-reactivated carbon fabric



time, min

Figure 10. HD penetrationFreon 113-contaminated and iodine-reactivated carbon fabric

Table 6. HD penetration test results: Toyobo fabric; different contaminant groups

IBS Sample Code	Battelle Sample Number	Contaminant Group	Reactivation Process*	Adjusted Breaktime (min)	Cumulative Penetration ($\mu g/cm^2$)	Cumulative Lapsed Time (min)
B12L	9H	None (control)	None		0.34	9000
L22A	13H	None (control)	None		0.32	9000
A32B	17H	None (control)	None		0.30	9000
C01	C01	None (control)	None		3.4	9210
C02	C02	None (control)	None		0.80	9660
CE013	CE013	None (control)	None		0.28	9000
GC019	GC019	None (control)	None		0.18	9120
GA1	GA1	Gasoline	None	3016	7.18	3570
GA2	GA2	Gasoline	None	1862	6.44	1440
GA3	GA3	Gasoline	None	3758	11.1	3570
G11A	1H	Gasoline	L,I,M		0.72	9000
A23S	10H	Gasoline	L,I,M		1.09	9000
S32G	14H	Gasoline	L,I,M		1.33	9000
EX1	EX1	Engine Exhaust	None	5358	8.5	7110
EX1	EX2	Engine Exhaust	None		2.65	9210
EX3	EX3	Engine Exhaust	None		1.75	9210
X23H	2H	Engine Exhaust	L,I,M		0.60	9000
E14X	15H	Engine Exhaust	L,I,M		0.62	9000
H35E	20H	Engine Exhaust	L,I,M		0.77	9000
DI1	DI1	Diesel Fuel	None	< 450	7.0	450
DI2	DI2	Diesel Fuel	None	< 450	7.6	450
DI3	DI3	Diesel Fuel	None	< 450	8.1	450
SXD2	SXD2	Diesel Fuel	L,S,M		3.6	9660
VDS5	VDS5	Diesel Fuel	L,S,M		3.0	9660
DSQ20	DSQ20	Diesel Fuel	L,S,M	9158	4.7	9600
E31D	3H	Diesel Fuel	L,I,M		1.58	9000
I27E	11H	Diesel Fuel	L,I,M		1.48	9000
D12E	21H	Diesel Fuel	L,I,M		2.50	9000
CI1	CI1	Cigarette Smoke	None	5532	6.3	6150
CI2	CI2	Cigarette Smoke	None		0.39	9210
CI3	CI3	Cigarette Smoke	None		1.1	10200
KHM8	KHM8	Cigarette Smoke	L,S		0.63	9660
MRK16	MRK16	Cigarette Smoke	L,S		0.46	10080
GMK21	GMK21	Cigarette Smoke	L,S		0.71	9660
KMV9	KMV9	Cigarette Smoke	L,S,M		0.41	9660
MVK17	MVK17	Cigarette Smoke	L,S,M		0.36	9660
M210	4H	Cigarette Smoke	L,I,M		0.46	9000
033M	23H	Cigarette Smoke	L,I,M		0.76	9000
S130	24H	Cigarette Smoke	L,I,M		0.48	9000

(Con'd)

Table 6. HD penetration test results: Toyobo fabric; different contaminant groups *(Con'd)*

IBS Sample Code	Battelle Sample Number	Contaminant Group	Reactivation Process*	Adjusted Breaktime (min)	Cumulative Penetration ($\mu g/cm^2$)	Cumulative Lapsed Time (min)
SW1	SW1	Simulated Sweat	None		0.78	9210
SW2	SW2	Simulated Sweat	None		3.32	9210
SW3	SW3	Simulated Sweat	None	9053	3.97	9840
WAQ4	WAQ4	Simulated Sweat	L,S		0.48	9660
AYW14	AYW14	Simulated Sweat	L,S		1.50	9660
WXA22	WXA22	Simulated Sweat	L,S		0.53	9660
VWA6	VWA6	Simulated Sweat	L,S,M		1.22	9660
AVW7	AVW7	Simulated Sweat	L,S,M		1.13	9000
WVA18	WVA18	Simulated Sweat	L,S,M	8739	8.22	10080
W24E	6H	Simulated Sweat	L,I,M		0.46	9000
E34S	18H	Simulated Sweat	L,I,M		0.70	9000
S12W	19H	Simulated Sweat	L,I,M		0.62	9000
DE1	DE1	Detergent	None		0.69	9210
DE2	DE2	Detergent	None		0.63	9180
O11A	5H	Detergent	L,I,M		0.38	9000
A22P	12H	Detergent	L,I,M		0.46	9000
P31S	22H	Detergent	L,I,M		0.62	9000
FR1	FR1	Freon 113	None		0.74	9210
FR2	FR2	Freon 113	None		0.68	9210
FR3	FR3	Freon 113	None		1.47	9660
FQT1	FQT1	Freon 113	L,S		0.94	9660
TFB3	TFB3	Freon 113	L,S		0.73	9660
TNF11	TNF11	Freon 113	L,S		1.05	9660
VTF10	VTF10	Freon 113	L,S,M		0.97	9000
TVF12	TVF12	Freon 113	L,S,M		0.52	9660
TFV15	TFV15	Freon 113	L,S,M		0.59	9660
O31F	7H	Freon 113	L,I,M		1.05	9000
E230	8H	Freon 113	L,I,M		0.87	9000
F14E	16H	Freon 113	L,I,M		1.18	9000

* Reaction Process identification
L - Laundering with detergent
S - Washing in isopropyl alcohol and vacuum dry in 50°C oven
I - Iodine treatment
M - Microwave activation

3. CCl_4 vapor tests

a. Standard CCl_4 tests (starch-iodide bubblers) on Toyobo samples

In the present study, the standard dynamic CCl_4 adsorption tests (starch-iodide detection) were conducted at US Army Natick Research, Development and Engineering Center using on-site facilities, equipment, as well as existing test procedures. Three types of samples were analyzed which included samples fully contaminated with the non-hydrocarbon soils, reactivated samples, and uncontaminated control samples. The apparatus for standard CCl_4 tests has a four-port manifold and is capable of analyzing four samples simultaneously. In all tests conducted, at least one of the four stations was reserved for analyzing an uncontaminated control sample. The CCl_4 flow rate was measured at least twice a day using active-carbon-filled Schwartz tubes (once in the morning before initiation of tests and once in the afternoon at the conclusion of the last test). The average value was used in the calculation of CCl_4 adsorption. The various test specimens were prepared as follows:

(1) Uncontaminated controls - preconditioned in an airflow oven overnight at 50 °C;

(2) Contaminated samples - hung to dry in a fumehood, then dried in an airflow oven at 50 °C overnight;

(3) Reactivated samples - final drying in an airflow oven overnight at 50 °C.

The standard dynamic CCl_4 adsorption test with starch-iodide bubblers may give erroneous results in the presence of organic contaminants, which can prevent formation of the blue complex that iodine-iodide I_3^- forms with the starch amylose helix[15,16]. For this reason, only samples associated with detergent, simulated sweat and Freon 113 were tested by this method. Freon 113 was included in this group because it is so volatile that not much residue is expected to remain, especially since the sample is pre-conditioned in a 50°C oven overnight.

Results of the standard dynamic CCl_4 adsorption tests for samples that do not contain hydrocarbon residues are presented in Table 7. The average values for the dynamic CCl_4 adsorption data given in Table 7 are summarized in Table 8 for different contaminant groups.

Table 7. Standard dynamic CCl_4 tests (starch-iodide detection) of uncontaminated, contaminated, and reactivated samples (Toyobo)

Contaminant Group	Reactivation Process*	Test Station	Average CCl_4 Flow (mg/min)	True Breaktime (min)	CCl_4 Adsorption (mg/cm^2)
None (control)	---	1	7.1	42	3.0
Detergent	---	2	6.0	34	2.0
Detergent	---	3	6.0	31	1.9
Detergent	---	4	6.0	37	2.2
None (control)	---	1	5.1	51	2.6
Detergent	L	2	4.9	41	2.0
Detergent	L	3	4.9	30	1.5
Detergent	L	4	4.9	31	1.5
None (control)	---	1	4.4	55	2.4
Detergent	L,I,M	2	4.7	35	1.7
Detergent	L,I,M	3	5.0	33	1.7
Detergent	L,I,M	4	4.8	41	2.0
None (control)	---	1	7.1	47	3.3
Sweat	---	2	6.0	40	2.4
Sweat	---	3	6.0	32	1.9
Sweat	---	4	6.0	26	1.6
None (control)	---	1	5.1	53	2.7
Sweat	L	2	4.9	49	2.4
Sweat	L	3	4.9	35	1.7
Sweat	L	4	4.9	39	1.9
None (control)	---	1	5.6	55	3.1
Sweat	L,S	2	5.2	89	4.6
Sweat	L,S	3	4.8	52	2.5
Sweat	L,S	4	5.5	74	4.1
None (control)	---	1	4.2	61	2.6
Sweat	L,S	2	4.4	76	3.3
Sweat	L,S	3	4.9	65	3.2
Sweat	L,S	4	5.0	72	3.6
None (control)	---	1	5.2	55	2.9
Sweat	L,S,M	2	4.9	30	1.5
Sweat	L,S,M	3	5.0	7	0.4
Sweat	L,S,M	4	5.1	11	0.6
None (control)	---	1	5.3	53	2.8
Sweat	L,S,M	2	5.0	26	1.3
Sweat	L,S,M	3	5.4	21	1.1
Sweat	L,S,M	4	5.1	37	1.9 *(Con'd)*

Table 7. Standard dynamic CCl_4 tests (starch-iodide detection) of uncontaminated, contaminated, and reactivated samples (Toyobo) *(Con'd)*

Contaminant Group	Reactivation Process*	Test Station	Average CCl_4 Flow (mg/min)	True Breaktime (min)	CCl_4 Adsorption (mg/cm_2)
None (control)	---	1	4.2	60	2.5
Sweat	L,I,M	2	4.4	43	1.9
Sweat	L,I,M	3	4.9	34	1.7
Sweat	L,I,M	4	5.0	50	2.5
None (control)	---	1	6.3	54	3.4
Freon 113	---	2	5.5	60	3.3
Freon 113	---	3	6.0	17	1.0
Freon 113	---	4	5.0	54	2.7
None (control)	---	1	5.1	52	2.7
Freon 113	L	2	4.9	33	1.6
Freon 113	L	3	4.9	9	0.4
Freon 113	L	4	4.9	26	1.3
None (control)	---	1	5.4	46	2.5
Freon 113	L,S	2	5.0	103	5.2
Freon 113	L,S	3	5.0	85	4.3
Freon 113	L,S	4	5.8	88	5.1
None (control)	---	1	4.4	63	2.8
Freon 113	L,S	2	4.7	58	2.7
Freon 113	L,S	3	5.0	38	1.9
Freon 113	L,S	4	4.8	56	2.7
None (control)	---	1	5.3	53	2.8
Freon 113	L,S,M	2	5.0	29	1.5
Freon 113	L,S,M	3	5.4	20	1.1
Freon 113	L,S,M	4	5.1	26	1.3
None (control)	---	1	4.2	61	2.6
Freon 113	L,I,M	2	4.4	45	2.0
Freon 113	L,I,M	3	4.9	35	1.7
Freon 113	L,I,M	4	5.0	53	2.7

* Reactivation process identification
L - Laundering with detergent and vacuum dry in 50°C oven
I - Iodine treatment
M - Microwave activation
S - Washing in isopropyl alcohol and vacuum dry in 50°C oven

Table 8. Average values of dynamic CCl_4 adsorption by Toyobo samples, contaminated; after steps in the reactivation process (Standard test, starch-iodide detection)

Contaminant Group	Reactivation Process	Avg CCl_4 Adsorption (mg/cm^2)	Normalized Adsorption*
Detergent	None	2.0	0.68
Detergent	L	1.7	0.64
Detergent	L,I,M	1.8	0.75
Sweat	None	1.9	0.58
Sweat	L	2.0	0.74
Sweat	L,S	3.6	1.25
Sweat	L,S,M	1.1	0.40
Sweat	L,I,M	2.0	0.81
Freon 113	None	2.3	0.69
Freon 113	L	1.1	0.41
Freon 113	L,S	3.7	1.38
Freon 113	L,S,M	1.3	0.46
Freon 113	L,I,M	2.1	0.82

* Normalized against the CCl_4 adsorption of the control sample tested simultaneously.

The following observations can be made based on the data presented in Tables 7 and 8:

(1) There is a significant data scattering among Toyobo fabric samples subjected to identical contamination and treatments.

(2) There is also some data scattering associated with uncontaminated control samples (average CCl_4 adsorption = 2.8 mg/cm^2, standard deviation = 0.28 mg/cm^2).

(3) Apparent greater CCl_4 adsorption was observed for samples washed in isopropyl alcohol (sweat and Freon 113, identified by processes L and S). The later breaktime is probably caused by residual isopropanol in the carbon pores, despite the prolonged vacuum drying process at 50°C. During the test, CCl_4, which has a higher affinity for active carbon, can displace isopropyl alcohol, which acts like hydrocarbon in interfering with CCl_4 detection by starch-iodide[15,16].

b. Simplified CCl_4 tests (copper-flame detection) on Toyobo samples

Since volatile contaminants were found to interfere with the detection of penetration of CCl_4 by pyrolyzer / starch-iodide bubblers, a simplified dynamic CCl_4 adsorption test apparatus (Figure 2) was used to evaluate test specimens associated with hydrocarbon contaminants including gasoline, diesel fuel, cigarette smoke and engine exhaust. The CCl_4 flow rate was measured at least twice a day using active-carbon-filled Schwartz tubes. The average value was used in the calculation of CCl_4 adsorption. The correct settings of the rotameter type flow meters are manually maintained with full vigilance. The simplified CCl_4 tests were conducted at room temperature using piped air which passed through several filters and moisture traps before entering the test apparatus.

As described earlier, two separate breaktimes were recorded. The initial breaktime is defined as the elapsed time when green flame first appears, whereas the final breaktime is defined as the total elapsed time when the green flame becomes prominent and fills the space above the copper reaction plate. The difference between the initial and the final breaktime is extremely short for contaminated samples, relatively short for uncontaminated controls, and, in some cases, long for reactivated samples.

Results of the simplified dynamic CCl_4 adsorption tests are given in Table 9. The average values for the same data under different contaminant groups are summarized in Table 10.

Table 9. Simplified dynamic CCl_4 tests (copper-flame detection) adsorption of uncontaminated, contaminated, and reactivated samples (Toyobo)

Contaminant Group	Reactivation Process*	Average CCl_4 Flow (mg/min)	Breaktime Initial/Final (min)	CCl_4Adsorption Initial/Final (mg/cm^2)
None (control)	None	18.5	22 / 24	4.1 / 4.5
None (control)	None	12.7	35 / 37	4.5 / 4.7
None (control)	None	12.4	32 / 35	4.0 / 4.4
None (control)	None	16.3	22 / 25	3.6 / 4.0
None (control)	None	16.3	20 / 23	3.3 / 3.7
None (control)	None	16.3	21 / 23	3.4 / 3.8
Cigarette Smoke	None	10.1	29 / 34	3.0 / 3.4
Cigarette Smoke	None	12.9	27 / 33	3.5 / 4.2
Cigarette Smoke	None	12.9	26 / 29	3.4 / 3.8

(Con'd)

Table 9. Simplified dynamic CCl_4 tests (copper-flame detection) adsorption of uncontaminated, contaminated, and reactivated samples (Toyobo) *(Con'd)*

Contaminant Group	Reactivation Process*	Average CCl_4 Flow (mg/min)	Breaktime Initial/Final (min)	Ccl4 Adsorption Initial/Final (mg/cm^2)
Cigarette Smoke	L	12.7	21 / 26	2.7 / 3.7
Cigarette Smoke	L	12.7	18 / 21	2.3 / 2.7
Cigarette Smoke	L	12.9	20 / 22	2.6 / 2.9
Cigarette Smoke	L,S	12.7	13 / 15	1.7 / 1.9
Cigarette Smoke	L,S	12.7	16 / 18	2.1 / 2.3
Cigarette Smoke	L,S	12.9	13 / 17	1.7 / 2.2
Cigarette Smoke	L,S,M	12.7	6 / 16	0.7 / 2.0
Cigarette Smoke	L,S,M	12.7	3 / 14	0.3 / 1.8
Cigarette Smoke	L,S,M	12.9	0.8 / 11	0.1 / 1.4
Cigarette Smoke	L,S,M	12.4	6 / 11	0.7 / 1.4
Cigarette Smoke	L,S,M	12.4	6 / 12	0.7 / 1.5
Cigarette Smoke	L,S,M	12.4	6 / 15	0.7 / 1.8
Cigarette Smoke	L,I,M	11.4	26 / 31	3.0 / 3.6
Cigarette Smoke	L,I,M	11.4	34 / 39	3.9 / 4.5
Cigarette Smoke	L,I,M	10.9	32 / 39	3.6 / 4.3
Gasoline	None	18.5	1.2 / 1.2	0.2 / 0.2
Gasoline	None	10.1	0.9 / 0.9	0.1 / 0.1
Gasoline	None	10.1	1.5 / 1.5	0.2 / 0.2
Gasoline	L	12.9	0.9 / 0.9	0.1 / 0.1
Gasoline	L	12.9	0.9 / 0.9	0.1 / 0.1
Gasoline	L	12.9	1.1 / 1.1	0.2 / 0.2
Gasoline	L,S	15.6	15 / 21	2.3 / 3.3
Gasoline	L,S	15.6	15 / 20	2.3 / 3.2
Gasoline	L,S	15.6	17 / 21	2.6 / 3.2
Gasoline	L,I,M	11.4	25 / 30	2.9 / 3.5
Gasoline	L,I,M	10.9	28 / 35	3.1 / 3.9
Gasoline	L,I,M	10.9	29 / 36	3.2 / 3.9

(Con'd)

Table 9. Simplified dynamic CCl_4 tests (copper-flame detection) adsorption of uncontaminated, contaminated, and reactivated samples (Toyobo) *(Con'd)*

Contaminant Group	Reactivation Process*	Average CCl_4 Flow (mg/min)	Breaktime Initial/Final (min)	CCl_4 Adsorption Initial/Final (mg/cm^2)
Diesel Fuel	None	18.5	0.2 / 0.2	0.03 / 0.03
Diesel Fuel	None	10.1	0.4 / 0.4	0.04 / 0.04
Diesel Fuel	None	10.1	0.6 / 0.6	0.06 / 0.06
Diesel Fuel	L	12.9	0.3 / 0.3	0.04 / 0.04
Diesel Fuel	L	12.9	0.4 / 0.4	0.05 / 0.05
Diesel Fuel	L	12.9	0.3 / 0.3	0.04 / 0.04
Diesel Fuel	L,S	12.9	4.0 / 4.5	0.5 / 0.6
Diesel Fuel	L,S	12.9	4.3 / 4.3	0.6 / 0.6
Diesel Fuel	L,S	12.9	5.6 / 5.6	0.7 / 0.7
Diesel Fuel	L,S,M	12.7	5.2 / 5.2	0.7 / 0.7
Diesel Fuel	L,S,M	12.7	7.3 / 7.3	0.9 / 0.9
Diesel Fuel	L,S,M	12.9	18 / 21	2.3 / 2.6
Diesel Fuel	L,S,M	12.4	15 / 21	1.9 / 2.6
Diesel Fuel	L,S,M	12.4	9 / 12	1.1 / 1.5
Diesel Fuel	L,I,M	10.9	5 / 16	0.5 / 1.8
Diesel Fuel	L,I,M	11.4	17 / 24	1.9 / 2.8
Diesel Fuel	L,I,M	11.4	11 / 16	1.2 / 1.8
Engine Exhaust	None	12.9	29 / 30	3.7 / 3.9
Engine Exhaust	None	12.9	32 / 33	4.2 / 4.3
Engine Exhaust	L	12.9	33 / 35	4.3 / 4.5
Engine Exhaust	L,I,M	10.9	17 / 28	1.8 / 3.0
Engine Exhaust	L,I,M	11.4	8 / 16	0.9 / 1.8
Engine Exhaust	L,I,M	11.4	11 / 18	1.2 / 2.0

* Reactivation process identification
L - Laundering with detergent and vacuum dry in 50 °C oven
I - Iodine treatment
M - Microwave activation
S - Washing in isopropyl alcohol and vacuum dry in 50 °C oven

Table 10. Average values simplified dynamic CCl_4 adsorption tests on Toyobo samples (Copper flame detection)

Contaminant Group	Reactivation Process	Average CCl_4 Adsorption Initial/Final (mg/cm^2)	Normalized* CCl_4 Adsorption Initial/Final (mg/cm^2)
None (control)	None	3.8 / 4.2	1.0 / 1.0
Cigarette Smoke	None	3.3 / 3.8	0.87 / 0.91
Cigarette Smoke	L	2.5 / 3.0	0.67 / 0.71
Cigarette Smoke	L,S	1.8 / 2.1	0.48 / 0.51
Cigarette Smoke	L,S,M	0.5 / 1.7	0.14 / 0.39
Cigarette Smoke	L,I,M	3.5 / 4.1	0.92 / 0.98
Gasoline	None	0.2 / 0.2	0.04 / 0.04
Gasoline	L	0.1 / 0.1	0.04 / 0.04
Gasoline	L,S	2.4 / 3.2	0.63 / 0.77
Gasoline	L,I,M	3.1 / 3.8	0.81 / 0.90
Diesel Fuel	None	0.04 / 0.04	0.01 / 0.01
Diesel Fuel	L	0.04 / 0.04	0.01 / 0.01
Diesel Fuel	L,S	0.6 / 0.6	0.16 / 0.15
Diesel Fuel	L,S,M	1.4 / 1.6	0.36 / 0.38
Diesel Fuel	L,I,M	1.2 / 2.1	0.32 / 0.51
Engine Exhaust	None	4.0 / 4.1	1.04 / 0.98
Engine Exhaust	L	4.3 / 4.5	1.13 / 1.07
Engine Exhaust	L,I,M	1.3 / 2.3	0.34 / 0.54

* Normalized against the control

Based on the data presented in Table 10, the following observations are made:

(1) CCl_4 adsorption determined by the simplified (copper-flame) method is higher than from the standard (starch-iodide) method, as evidenced by the values obtained for uncontaminated control samples. The challenge used in the simplified test is 15 mg/L, while standard tests were done at a 5 mg/L challenge concentration. A later study shows that the shift up from 5 mg/L challenge concentration might produce at least some of the effect. The higher sensitivity of starch-iodide also gives earlier breakthrough detection.

(2) Despite the very strong, lingering smell, the adsorptive property of Toyobo fabric diminishes only slightly as a result of cigarette smoke contamination. It is possible that the particle size of cigarette smoke is relatively large so that the smoke deposits do not penetrate deep into the micropores of the active carbon. Being a small molecule, CCl_4 can still be adsorbed readily and effectively.

(3) The adsorptive property of cigarette smoke-contaminated samples worsens progressively when they are washed in detergent solution and isopropyl alcohol. The yellow stain deposited by cigarette smoke is soluble in warm water and isopropanol. It is conceivable that by washing in water or alcohol, the large size smoke deposits may dissolve and spread into the micropores, resulting in secondhand contamination of the microsurfaces. The adsorptive capacity is however restorable with the use of iodine as a displacing agent (Table 11). This is consistant with the experimental observation that the cigarette smell can be eliminated completely only through the use of iodine.

(4) Because of its low surface tension, gasoline can penetrate micropores readily and fouling of the macro- and microsurfaces is complete. As a result, the capacity to adsorb CCl_4 is almost zero. Gasoline does not dissolve in water and washing in detergent solution is not at all effective. However, because gasoline is somewhat soluble in isopropanol, washing in this solvent does restore some absorptive capacity. Further restoration was achieved with iodine activation (80 to 90%).

(5) The contamination of diesel fuel is qualitatively similar to gasoline; however, both isopropanol and the iodine activation failed to substantially restore the CCl_4 adsorption capacity. This is because diesel fuel is much less miscible with iso-propanol than gasoline. The 70% isopropanol solvent selected for iodine activation is not effective in the case of diesel fuel.

(6) The enhancement of CCl_4 adsorption by engine exhaust deserves further stüdy. When the sample was wetted with isopropanol, dynamic breaktime was shortened. Smaller particles than in cigarette smoke appear to become lodged in pores. They interfere with access of CCl_4 test vapor.

c. Static CCl_4 adsorption test

Static CCl_4 adsorption tests were routinely performed for quick assessment of performance and quality control. The CCl_4 sorptivity of samples from the same batch of fully reactivated (identified by processes L,I,M) samples used for GD and HD tests is summarized in Table 11. Additional static adsorption data are given in the next section.

Table 11. Static CCl_4 adsorption of fully reactivated Toyobo fabric samples

Contaminant Group	CCl_4 Adsorbed Per* Unit Fabric Weight, %	Average %	Normalized** Activity Relative to Control
Uncontaminated Control	19.3		
	19.8		
	21.2		
	19.8	20.0	1.00
Detergent	22.3		
	22.5		
	22.7		
	22.2	22.4	1.12
Simulated Sweat	23.4		
	22.0		
	22.8		
	21.8	22.5	1.13
Cigarette Smoke	22.1		
	23.7		
	23.0		
	22.4	22.8	1.14
Engine Exhaust	20.7		
	23.2		
	20.4		
	21.7	21.5	1.08
Gasoline	21.0		
	20.3		
	20.1		
	20.8	20.6	1.03
Diesel Fuel	16.7		
	15.4		
	15.6		
	16.0	15.9	0.80
Freon 113	20.8		
	19.9		
	21.1		
	18.7	20.1	1.01

* Excluding shell fabric
** Normalized against control

4. Combined data

a. Summary of all test data

In this section, the experimental adsorption data obtained via the live agent vapor tests, the standard and the simplified dynamic CCl_4 tests, and the "static" (equilibrium) CCl_4 test are all tabulated together.

In Table 12, the first column lists the contaminant groups, the second identifies the reactivation processes involved, the third and the fourth columns tabulate the average 150-hour cumulative penetration of GD and HD, respectively. Because some of the HD permeation tests extended beyond the required time span, some of the data were obtained by interpolation. In cases where the breakthrough criteria (10 μg/cm for GD and 4 μg/cm^2 for HD) were surpassed, the 150-hour cumulative penetration values were not recorded and therefore not shown. The number of fabric samples which broke through before the end of the 150-hour test period is given in parenthesis (with 3/3 denoting three out of three samples).

The fifth column lists the normalized CCl_4 adsorption against the uncontaminated control for samples tested by the standard dynamic CCl_4 adsorption test[1b] (starch-iodide detection), whereas the sixth column lists the normalized adsorption based on the simplified method[5] (copper-flame detection), including both values associated with the initial and the final breakpoint criteria defined earlier. The last column likewise gives the normalized values from static equilibrium CCl_4 tests.

Table 12. Summarized evaluation of steps in the cleaning and reactivation of the Toyobo ensemble of activated fiber carbon fabric

Contaminant Group	Reactivation Process*	150-hour Penetration GD (mg/cm^2)	HD	CCl_4 Adsorption Tests (Reduced [vs. Controls]) Standard	Simplified	Static
None (control)	None	0.02	0.79	1.0	1.0/1.0	1.0
Gasoline	None		Brk 62h (3/3)		0.04/0.04	
Gasoline	L				0.04/0.04	0.15
Gasoline	L,S				0.63/0.77	0.90
Gasoline	L,I,M	0.0	1.05		0.81/0.90	1.03
Engine Exhaust	None		Brk 89h (1/3)		1.04/0.98	1.10
Engine Exhaust	L				1.13/1.07	1.10
Engine Exhaust	L,I,M	0.16	0.66		0.34/0.54	1.08
Diesel Fuel	None		Brk 7h (3/3)		0.01/0.01	
Diesel Fuel	L				0.01/0.01	0.05
Diesel Fuel	L,S				0.16/0.15	0.20
Diesel Fuel	L,S,M		2.77		0.36/0.38	0.40
Diesel Fuel	L,I,M	0.17	1.85		0.32/0.51	0.80
Cigarette Smoke	None		Brk 92h (1/3)		0.87/0.91	0.75
Cigarette Smoke	L				0.67/0.71	0.60
Cigarette Smoke	L,S		0.46		0.48/0.51	0.45
Cigarette Smoke	L,S,M		0.30		0.14/0.39	0.90
Cigarette Smoke	L,I,M	0.02	0.57		0.92/0.98	1.14
Simulated Sweat	None		2.41	0.58		0.65
Simulated Sweat	L			0.74		0.70
Simulated Sweat	L,S		0.65	1.25		0.75
Simulated Sweat	L,S,M		Brk 135h (1/3)	0.40		0.80
Simulated Sweat	L,I,M	0.08	0.59	0.81		1.13
Detergent	None		0.62	0.68		0.90
Detergent	L			0.64		0.75
Detergent	L,I,M	0.05	0.49	0.75		1.12
Freon 113	None		0.84	0.69		1.0
Freon 113	L			0.41		0.70
Freon 113	L,S		0.74	1.38		0.80
Freon 113	L,S,M		0.63	0.46		0.55
Freon 113	L,I,M	1.97	1.03	0.82		1.01

* Reactivation process identification
L - Laundering with detergent and vacuum dry in 50 °C oven
I - Iodine treatment
M - Microwave activation
S - Washing in isopropyl alcohol and vacuum dry in 50 °C oven

b. Normalized HD penetration and CCl_4 adsorption test data

These data are contrasted by the display in Figure 11. The HD penetration, the dynamic CCl_4 adsorption, and the static CCl_4 activity, all of them normalized against the respective control values, are graphically presented. The performance level of control samples is marked by an arrow pointing at the numerical value 1.

The normalized HD penetration is indicated by the inverted scale on the left hand side. Since a lower penetration reflects a greater sorptive power, the height of the curve represents the performance of the reactivation process.

The normalized CCl_4 adsorptions are indicated by the scale on the right hand side. Since a higher adsorption reflects a greater sorptive power, the height of the curve again represents the performance of the specific process. For values above 1, the performance exceeds that of the control samples.

The arbitrary horizontal scale of Figure 11 represents the level of regeneration. The process corresponding to the lowest level on the left hand side is designated as "soiled", meaning that the test samples are merely contaminated and no reactivation is performed. The symbols for the various reactivation processes are identical to those of Table 12. The performance of samples subjected to the full reactivation processes is shown on the right hand side.

A brief discussion of the various test results is given below.

C. DISCUSSION

1. Assessment of reactivation by iodine in aqueous isopropanol

a. Soman (GD) vapor penetration

Throughout the entire 150-hour test period, breaklevel penetration was not observed in any of the samples subjected to the full reactivation processes. Based on the cumulative breakthrough data, the iodine reactivated samples are by and large up to par in performance with the control samples. Residual Freon 113 apparently permits slightly greater GD penetration.

b. Mustard (HD) vapor penetration

i. Over the 150-hour test period, none of the fully reactivated samples (identified by processes L,I,M) reached the standard cumulative breaklevel criterion for HD ($4\mu g/cm^2$).

ii. Breakthrough occurred in all three triplicate samples contaminated with gasoline or diesel fuel, and in one of each of the triplicate samples contaminated with engine exhaust, cigarette smoke, or simulated sweat

iii. Breakthrough was not observed in samples contaminated with Type II detergent and Freon 113.

iv. Partially reactivated samples (identified by processes L.S or L.S.M) generally have less adsorptive capacity when compared to fully reactivated samples.

v. The fully reactivated samples, although not as good as the control in every case, are about equivalent in performance. The Phase II-A reactivation processes, therefore, show good promise as viable methods for reactivation of carbon fabrics for chemical protection.

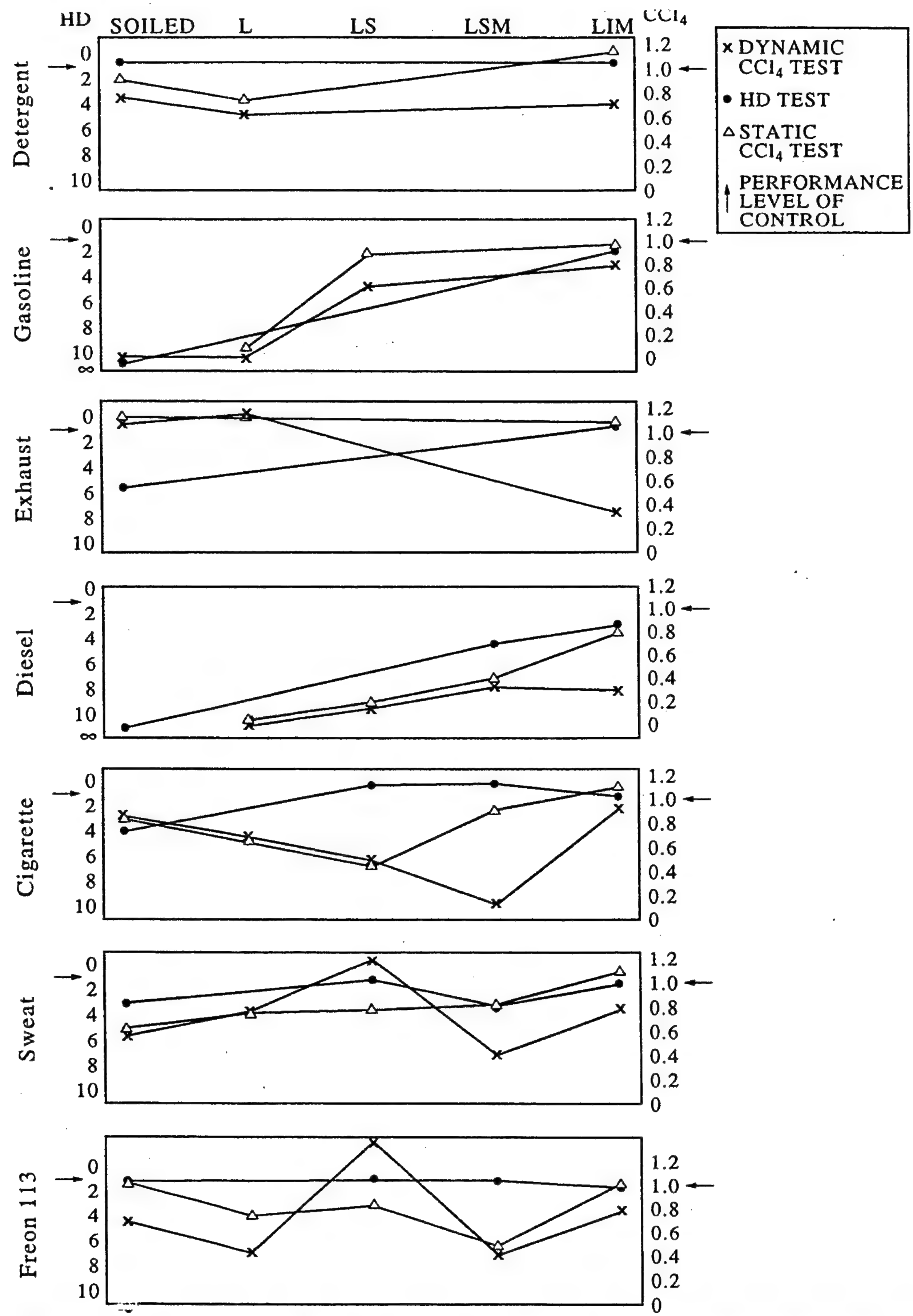


Figure 11. Summary graphs of HD and CCl_4 tests on Toyobo samples contaminated and reactivated to various extents

c. Standard dynamic CCl_4 adsorption test (Pyrolyzer/starch-I^- assay)

i. Even though carbon loss is not a problem there is significant dynamic sorption data scatter among Toyobo fabric samples subjected to identical contamination and treatments.

ii. There is also some data scattering associated with uncontaminated control samples (average CCl_4 adsorption = 2.8 mg/cm^2, standard deviation = 0.28 mg/cm^2).

iii. Seemingly paradoxical enhancement in dynamical CCl_4 adsorption was observed in samples washed in isopropyl alcohol (sweat and Freon 113, identifiedby processes L and S), in standard tests with starch-iodide detection. Isopropanol residue is one plausible explanation, despite the prolonged vacuum drying process at 50°C. Since CCl_4 has a great affinity for active carbon, it may, during the test, displace adsorbed isopropyl alcohol, which interferes with starch- iodide detection. The saturated capacity (below (e)) has not increased.

d. Simplified Dynamic CCl_4 Adsorption Test (Flame Assay)

i. The CCl_4 adsorption resulting from the simplified method is higher than from the standard method as evidenced by values obtained by both methods on uncontaminated control samples. Two causes can be cited: flame detection is less sensitive than starch-iodide, and, it was found in later studies that at the lower challenge rate around 4 mg/min, breakthrough occurs at distinctly lower cumulative sorption, with a large scatter in the values, than for the simplified test challenge of 15 mg/min. The challenge in standard tests was 5 mg/L.

ii. Despite the very strong, lingering smell, the adsorptive property of Toyobo fabric diminishes only slightly as a result of severe cigarette smoke contamination. It is possible that the particle size of cigarette smoke deposits is relatively large so that these smoke deposits do not penetrate deep into the micropores of the active carbon. Being small in size, the CCl_4 molecules can still be adsorbed readily and effectively in a dynamic test. However:

iii. Instead of improving, the adsorptive property of cigarette smoke- contaminated samples worsens progressively with the degree of reactivation, such as washing in detergent solution and in 70% isopropyl alcohol, at room temperature. It is conceivable that the large size smoke deposits may have been floated into the micropores, resulting in secondhand contamination of the microsurfaces. The adsorptive capacity is restorable with the use of iodine as a displacing agent (Table 12). This is consistant with the experimental observation that the cigarette smell was not eliminated completely before the use of iodine.

iv. Because of its low surface tension, gasoline can penetrate micropores readily so that fouling of the macro- and micro- surfaces is complete. As a result, the capacity to absorb CCl_4 is almost zero. Because gasoline does not dissolve in water, washing in detergent solution is not at all effective. However, because gasoline is soluble in isopropanol, the washing in 70% isopropanol did restore some adsorptive capacity. Further restoration of CCl_4 adsorption was achieved with iodine displacement (80 to 90% of original sorptivity).

v. The contamination of diesel fuel is qualitatively similar to gasoline except that both isopropanol and the iodine activation failed to substantially restore the CCl_4 adsorption capacity. This is because diesel fuel is much less miscible with isopropanol than gasoline. A contaminant can be displaced by iodine only if

surrounded by solvent; the selected system (water/isopropanol mixture) is not a good enough solvent in the case of diesel fuel.

vi. The anomalous enhancement of CCl_4 adsorption in the case of engine exhaust is difficult to explain. When the sample was wetted with isopropanol, dynamic breaktime was shortened, but when subsequently challenged to equilibrium (see below), gave the enhanced value. Particles, perhaps smaller than in cigarette smoke, appear to become lodged in pores. They interfere with access of CCl_4 test vapor. Further study is required.

e. Equilibrium ("static") CCl_4 adsorption test

The static CCl_4 activity appears to correlate better with live agent penetration performance than with CCl_4 adsorption obtained via dynamic standard and simplified dynamic tests (Figure 11). The shorter dynamic CCl_4 test is more stringent, since displacement by the test vapor is possible in both the 150-hour dynamic HD test and the equilibrium saturation CCl_4 test.

f. Microwave drying

There is no indication of enhancement in sorptivity after microwave drying of Toyobo samples. The effect is apparently specific for impregnated foam, in which activated carbon particles are bound by acrylic polymer.

2. Assessment of procedures in Phase IIA

a. Contamination procedure

In Phase II-A investigation, selected contaminants were separately applied to the test material in a controlled, reproducible manner. In order to assess the true efficacy of the reactivation process, efforts were made to apply each contaminant to the utmost extent, that is, in a manner far more severe than ever expected in real life to ensure maximum coverage, full penetration, saturation and complete soiling by the contaminant. Therefore, the performance of the reactivated sample would be far superior if the contaminants were applied in a realistic manner. Over the 150-hour test period, all of the reactivated test specimens resisted penetration at breakthrough levels set for soman and mustard vapors. Although the performance of reactivated samples was not as good as the control in every case, the technique did show good promise of being a viable method for reactivation and rejuvenation of active carbon materials. Results in Phase II-A have provided a reasonable foundation for further refinement of the technique.

b. Laundering temperature

In conformance to standard practice adopted for conventional military laundry equipment, the water temperature for the detergent wash cycle was chosen to be approximately 90 °F. However, evidence based on simple bench tests suggests that a higher temperature is more beneficial because:

(1) Although basically hydrophilic, some sweat residues, such as leucine and other equivalent amino acids, dissolve very slowly in water at 90 °F. At a slightly higher temperature such as 130 F, leucine will dissolve almost instantly;

(2) The yellow stain deposited on the material by cigarette smoke can not be readily removed via a 90 °F detergent wash process. At a higher temperature such as 130 °F, the same stain can be removed more effectively during the detergent laundering cycle.

However, the optimal temperature for the detergent wash cycle remains to be explored in future studies.

c. The iodine displacement solvent

In the present application, iodine was used in aqueous/organic solvent, in which it has limited solubility, to facilitate its adsorption at the solid surface. Yet the adsorbed hydrocarbon soil requires a good solvent so that it may leave the surface. The introduction of isopropanol has the bonus effect of reducing the surface tension of the solution, allowing micropores to fill without resorting to vacuum evacuation.

In retrospect, mixing water with the isopropanol may be unwise. While the removal of water soluble contaminants was enhanced, the displacement of water insoluble contaminants was hindered. A more effective strategy might be to dissolve iodine separately in isopropanol and in water. The iodine-in-isopropanol solution should be introduced first to displace water-insoluble contaminants. Immediately following this step the iodine-in-water solution could be introduced in order to dislodge hydrophilic contaminants. The aqueous iodine solution is capable of penetrating the deep micropores in spite of its intrinsic high surface tension, because the preceding isopropanol solution has already wetted the surface, and dislodged all entrapped air, by virtue of its low surface tension.

Finally, in place of isopropanol, other more powerful solvents or (nonaqueous) solvent mixtures can also be used. Freon 113, miscible with gasoline and diesel fuel, is expected to be even more effective than isopropanol. Iodine can dissolve readily in either isopropanol or Freon 113 at moderately elevated temperature.

The efficacy of iodine treatment can be confirmed qualitatively. In the case of cigarette smoke contamination, the strong cigarette smell lingers despite repeated wash in detergent solution, isopropyl alcohol, or Freon 113. The cigarette odor was eliminated completely only by washing in an iodine/water/isopropanol solution followed by the iodine removal step involving sodium thiosulfate.

Note: it should be mentioned that soaking in diesel fuel tends to cause the Toyobo carbon fabric layer to separate and delaminate. Gasoline and Freon 113 also have the same effect although to a lesser degree. Apparently, such solvents are capable of dissolving the thermobonding adhesive used in the Toyobo composite fabric material.

3. Assessment of test methods

a. Delayed end-point

In the presence of certain contaminants such as gasoline, diesel fuel, cigarette smoke and engine exhaust, unrealistically long breaktimes were found, using blue coloration in starch-iodide bubblers. Pyrolysis of CCl_4 forms Cl· radicals which are carried to the bubbler and oxidize iodide ions to iodine. We considered that hydrocarbon radicals might scavenge the chlorine radicals. However, it is known that starch iodide detection fails in the presence of hydrocarbons because iodine is reactive to hydrocarbons (Treadwell)[16]; also organic solvent interferes with formation of the blue starch-I_3^- complex (Bishop)[16]. With the color change of the starch indicator solution retarded, an incorrect long breaktime is seen.

b. Solvent removal from samples after reactivation

Seemingly paradoxical enhancement in adsorption by standard tests with starch-iodide detection was observed in samples that underwent isopropanol wash (Table 7 and 8, data for sweat and Freon 113), despite the prolonged vacuum drying process at 50 °C. Regeneration studies at Natick have shown that in an oven in the absence of convective air flow, the emptying of deep pores is a very slow process, even above the boiling point of the sorbed liquid[18a].

c. Leak-tight test cups

In the present study, a minor modification of the standard specimen cup was required. It was discovered that an appreciable amount of room air can be drawn into the Dawson cup through the rims where metal and test material were compressed together. The leakage was especially serious for the Toyobo material due to its piled surface, thickness, and fiber-knit construction, in spite of the clamping action provided by a large "C" clamp. The leakage problem was solved by installation of rubber gaskets.

Therefore, direct application of the standard CCl_4 adsorption test[1b] should be with caution in the following cases:

(1) Presence of volatile organic contaminants on the test material.
(2) Presence of trace organic solvent
(3) Possibility of air leakage at the interface between metal and test material

The above concerns do not apply to live agent tests because 1. wax seal of the specimen cup is a standard practice, and 2. penetration of chemical agents is measured by agent-specific gas chromatography of bubbler solution.

d. Agent tests vs. CCl_4 tests, dynamic and static

Through live agent tests, the fully reactivated active carbon fabric specimens were found to be up to par in performance with the fresh, uncompromised material. Over the 150-hour test period, none of the reactivated samples reached the breakthrough criteria of GD and HD.

Live agent tests (HD) were performed on various contaminated, partially reactivated, and uncompromised control samples. As expected, breakthrough was observed in contaminated samples containing residues of diesel fuel, gasoline, engine exhaust, cigarette smoke and simulated human sweat. However, samples contaminated with Freon 113 and Type II detergent did not reach the breakthrough criterion of HD. In the absence of iodine treatment, the various partially reactivated samples generally exhibited mediocre and inferior performance.

In some cases, the superior performance of the fully reactivated samples confirmed through live agent tests was not corroborated by the dynamic CCl_4 adsorption tests:

The CCl_4 adsorption (Table 11) established through static tests were found to be more consistent with the performance based on live agent tests. With the exception of diesel fuel contaminated samples, the static CCl_4 adsorption for fully reactivated samples is always equal to or better than that of the uncontaminated control.

That dynamic breakthrough of CCl_4 occurs relatively earlier for the soiled and reactivated samples, whereas CCl_4 equilibrium sorption was not less than control samples' (unless the contaminant was diesel fuel), suggests the CCl_4 test vapor can slowly displace moderately volatile contaminants that remain in the pores.

The good performance of reactivated samples in agent tests might also be in part due to displacement by the strong adsorber molecules of agent, applied over a 150-hour span.

4. Effective features

Future work will utilize the following effective factors and determine how they can be optimized:

(1) Use of iodine, a strong displacing agent for desorption of a broad spectrum of contaminants. Iodine has a very small molecular diameter and can penetrate carbon micropores with large adsorbed contaminants;

(2) Use of isopropanol whose surface tension allows rapid penetration to micropores, yet is a solvent for polar soils;

(3) Use of nonaqueous solvents in which potential battlefield contaminants, including long hydrocarbon chains and aromatics, are soluble;

(4) Use of vacuum evaporation to enhance vapor phase desorption of volatile contaminants;

(5) Use of microwave drying after water rinse, for AC/ impregnated foam;

(6) While reactivation by the proposed technique appeared to have been confirmed by live agent tests, results of dynamic CCl_4 adsorption tests failed to corroborate the performance in all cases. A number of plausible explanations were discussed and further investigation is warranted.

VII. PHASE IIB REACTIVATION WITH NONAQUEOUS IODINE SOLUTIONS

The criteria for a potential solvent candidate can be summarized as follows:

(1) High solubility for various contaminants especially diesel fuel and gasoline;

(2) Low affinity, low adsorptivity and low retentivity for active carbon, or alternatively, ease of residue removal via simple physical means;

(3) Having a boiling point above normal ambient temperature in order to remain in a liquid state;

(4) Having a relatively low boiling point for achieving low energy recovery and recycling;

(5) Acceptable iodine solubility (although not definitive, test results indicated that solvent alone without iodine is not capable of fully regenerating the active carbon material: in Phase IIA isopropanol alone failed, and in Phase I the strong solvent perchloroethylene, which attacks Type III foam, did not fully regenerate diesel-soaked samples);

(6) High water solubility to facilitate the iodine removal step involving an aqueous sodium thiosulfate solution;

(7) Low surface tension and viscosity for ease of pore penetration and flow;

(8) Low toxicity, low carcinogenicity, low flammability, low cost; no environmental impact.

A. SURVEY OF 23 SOLVENTS

1. Physical properties: solubility of iodine and soils in solvents

Physical properties of potentially useful organic solvents have been compiled in Tables 13A i, ii, iii, and advantages or disadvantages for the present application are listed in Table 13B. Some of the common solvents,

which are not suitable for the present application, are also included for comparison and reference. Among these organic solvents, only ethanol and methanol were found to have very low solubility for diesel fuel, whereas all other organic solvents were found to be completely miscible with diesel fuel. For those Freon solvents that were not available for testing, excellent solubility for petroleum products was confirmed by the manufacturer. All organic solvent tested, including ethanol and methanol, were found to be completely miscible with gasoline and have sufficiently low surface tension to facilitate surface wetting and penetration of fine pores and crevices. Furthermore, these organic solvents were found to be miscible with one another.

Table 13A. Physical Properties of Some of the Potential Solvents

Table 13A (i)

Solvent	Formula	Molecular Weight	Boiling Point °C	Latent Heat of Vaporization K Cal/mole	Flash Point °C
Acetone	CH_3COCH_3	58	56	7.6	-18
Benzene	C_6H_6	78	80	10.	-11
Bromobenzene	C_6H_5Br	157	156	10.	51
Carbon Tetrachloride	CCl_4	154	77	8.3	Nonflammable
Chloroform	$CHCl_3$	119	62	7.5	Nonflammable
Methylene Chloride	CH_2Cl_2	85	40	7.6	Nonflammable
Perchloro-ethylene	$CCl_2\ CCl_2$	166	121	9.2	Nonflammable
Trichloro-ethylene	$CCl_2\ CHCl$	131	87	8.3	Nonflammable
1,1,1, Trichlo-roethane	CH_3CCl_3	133	74	8.0	Nonflammable
Toluene	$C_6H_5CH_3$	92	111	9.4	4.4
Xylene	$C_6H_4(CH_3)_2$	106	144	9.9	25
Hexane	C_6H_{14}	86	69	7.6	-
Heptane	C_7H_{16}	100	98	8.9	-1
Ethanol	CH_3CH_2OH	46	78	9.7	13
Methanol	CH_3OH	32	65	9.4	12
Isopropanol	$CH_3CH(OH)CH_3$	60	82	10.	12
Freon 11	Cl_3F	137	24	6.4	Nonflammable
Freon 21	$CHCl_2F$	103	8.9	6.3	Nonflammable
Freon 113	$C_2Cl_3F_3$	187	48	7.1	Nonflammable
Freon 114	$C_2Cl_2F_4$	171	4	6.1	Nonflammable
Freon 114 B2	$C_2Br_2F_4$	260	47	-	Nonflammable
Freon 132	$C_2H_2Cl_2F_2$	135	47	-	Nonflammable
Freon 123	$C_2HCl_2F_3$	153	26	-	Nonflammable
Water	H_2O	18	100	9.7	Nonflammable

(Con'd)

Table 13A. Physical Properties of Some of the Potential Solvents *(Con'd)*

Table 13A (ii)

Solvent	Surface Tension dynes/cm	Viscosity Centipoise	Molecular Dipole Moment	Solubility in Water
Acetone	24	0.32	2.9	Miscible
Benzene	29	0.65	0.	0.07
Bromobenzene	37	1.2	1.7	0.05
Carbon Tetrachloride	27	0.97	0.	0.05
Chloroform	27	0.58	1.0	0.5
Methylene Chloride	27	0.33	1.6	50.
Perchloro-ethylene	32	-	-	0.01
Trichloro-ethylene	29	-	-	0.
1,1,1, Trichlo-roethane	22	1.2	1.8	0.
Toluene	29	0.59	0.36	0.
Xylene	30	0.81	0.62	0.
Hexane	18	0.33	-	0.
Heptane	-	0.41	-	0.
Ethanol	23	1.1	1.7	Miscible
Methanol	23	0.55	1.7	Miscible
Isopropanol	22	2.1	1.7	Miscible
Freon 11	18	0.42	0.45	0.01
Freon 21	18	0.34	1.3	0.95
Freon 113	17	0.68	-	0.01
Freon 114	12	0.38	-	0.01
Freon 114 B2	18	0.72	-	-
Freon 132	-	-	-	0.01
Freon 123	-	-	-	-
Water	73	1.0	1.9	100.

(Con'd)

Table 13A. Physical Properties of Potential Solvents *(Con'd)*

Table 13A (iii)

Solvent	Diesel Fuel Solubility	Gasoline Solubility	Iodine Solubility	Acceptable Endurance Limit PPM	1992 PPM	Solubility for Cigarette Sample Residue
Acetone	Miscible	Miscible	Excellent	1000	750	Good
Benzene	Miscible	Miscible	Excellent	10	1	Fair
Bromobenzene	Miscible	Miscible	Excellent	-	-	Fair
Carbon Tetrachloride	Miscible	Miscible	Fair	10-25	2	Poor
Chloroform	Miscible	Miscible	Good	50	2	Fair
Methylene Chloride	Miscible	Miscible	Good	500	100	Good
Perchloro-ethylene	Miscible	Miscible	Fair	100	25	Fair
Trichloro-ethylene	Miscible	Miscible	Fair	100	50	Fair
1,1,1, Trichlo-roethane	Miscible	Miscible	Good	350	350	Good
Toluene	Miscible	Miscible	Good	200	100	Fair
Xylene	Miscible	Miscible	Good	100	100	Fair
Hexane	Miscible	Miscible	Fair	500	50	Poor
Heptane	Miscible	Miscible	Fair	500	400	Poor
Ethanol	0	Miscible	Good	1000	1000	Excellent
Methanol	0	Miscible	Good	200	200	Excellent
Isopropanol	Miscible	Miscible	Good	400	400	Excellent
Freon 11	Miscible	Miscible	Poor	1000	-	None
Freon 21	-	-	-	200	-	-
Freon 113	Miscible	Miscible	Poor	1000	-	None
Freon 114	-	-	-	1000	-	-
Freon 114 B2	-	-	-	-	-	-
Freon 132	-	-	-	-	-	-
Freon 123	-	-	-	100	10	-
Water	0	0	Good*	Not Toxic		Poor**

* With KI as a solubilizing salt.
** Good at high temperature such as at 54° C.

Pertaining to the present application, the advantages and disadvantages of various potential solvents are summarized as follows.

Table 13B. Summary of Advantages and Disadvantages, Potential Solvents Table 13A

(1) Acetone (Dimethyl Ketone)

Advantages:

(A) a strong solvent for fats, oils, petroleum products, resins, waxes, lacquers, varnishes, rubber, and certain plastics,

(B) low boiling point, low latent heat of vaporization for low energy recovery and recycle,

(C) miscible with water and other organic solvents,

(D) excellent solubility for iodine.

Disadvantage:

(A) highly flammable.

(2) Benzene

Advantages:

(A) a strong solvent for oils and organic compounds,

(B) miscible with most solvents and petroleum fuels,

(C) excellent solubility for iodine.

Disadvantages:

(A) carcinogenic,

(B) highly flammable,

(C) low solubility in water.

(3) Bromobenzene

Advantages:

(A) a strong, heavy, industrial solvent,

(B) miscible with motor oils and organic solvents,

(C) excellent solubility for iodine.

Disadvantages:

(A) low solubility in water,

(B) high cost.

(4) Carbon Tetrachloride

Advantages:

(A) a strong solvent,

(B) miscible with oils and other organic solvent,

(C) nonflammable,

(D) high affinity for active carbon (a potential displacing agent).

Disadvantages:

(A) carcinogenic,

(B) low solubility for water and iodine,

(C) affinity for active carbon (residue or poisoning effect).

(5) Chloroform (Trichloromethane)

Advantages:

(A) a heavy cleansing agent, a strong solvent for fats, oils, rubber, waxes, resins, alkaloids etc.

(B) low boiling point, low latent heat of vaporization for low energy recovery,

(C) nonflammable,

(D) good solubility for iodine.

Disadvantages:

(A) toxic (an anesthetic and a carcinogen),

(B) light sensitive,

(C) affinity for active carbon (residue or poisoning effect).

(6) Methylene chloride (Dichloromethane)

Advantages:

(A) a degreasing and cleaning fluid,a solvent used in food processing,

(B) nonflammable,

(C) very low boiling point and low latent heat of vaporization for low energy recovery,

(Con'd)

Table 13B. Summary of Advantages and Disadvantages, Potential Solvents Table 13A *(Con'd)*

(6) Methylene chloride (Dichloromethane)

Advantages: (Con'd)
(D) good solubility for iodine and water,
(E) miscible with other organic solvents.

Disadvantages:
(A) affinity for active carbon (residue or poisoning effect)

(7) Perchloroethylene (Tetrachloroethylene)

Advantages:
(A) a standard dry cleaning fluid, a strong degreasing solvent,
(B) nonflammable.

Disadvantages:
(A) high boiling point and high latent heat of vaporization,
(B) poor solubility for water and iodine,
(C) affinity for active carbon (residue or poisoning effect).

(8) Trichloroethylene

Advantages:
(A) a strong solvent for fats, fixed and volatile oils, waxes, resins rubber, paints and varnishes, a degreasing and dry cleaning fluid,
(B) nonflammable.

Disadvantages:
(A) light sensitive,
(B) poor solubility for iodine and water,
(C) affinity for active carbon (residue or poisoning effect)

(9) 1,1,1,Trichloroethane (Methylchloroform)

Advantages:
(A) a popular cold cleaning fluid for metals and plastics,

(9) 1,1,1,Trichloroethane (Methylchloroform)

Advantages: (Con'd)
(B) nonflammable,
(C) good solubility for iodine.

Disadvantages:
(A) insoluble in water,
(B) affinity for active carbon (residue or poisoning effect).

(10) Toluene (Methylbenzene)

Advantages:
(A) a good slovent for paints, lacquers, gums, resins,
(B) good solubility for iodine.

Disadvantages:
(A) flammable,
(B) insoluble in water.

(11) Xylene (Dimethylbenzene)

Advantages:

(A) a popular organic solvent and cleaning agent,
(B) good solubility for iodine.

Disadvantages:
(A) insoluble in water,
(B) flammable.

(12) Hexane

Advantages:
(A) a good slovent for petroleum fuel,
(B) low boiling point, low latent heat of vaporization for ease of recovery.

Disadvantages:
(A) flammable,
(B) poor iodine and water solubility.

(Con'd)

Table 13B. Summary of Advantages and Disadvantages, Potential Solvents Table 13A *(Con'd)*

(13) Heptane

Advantages:
(A) a good solvent for petroleum fuel,
(B) low cost.

Disadvantages:
(A) poor solubility for iodine and water,
(B) flammable.

(14) Denatured Ethanol (Ethyl Alcohol)

Advantages:
(A) a popular industrial and laboratory solvent,
(B) good solubility for iodine,
(C) miscible with water and other organic solvents,
(D) ability to dissolve cigarette stains and smoke residues.

Disadvantages:
(A) extremely low solubility for diesel fuel,
(B) flammable.

(15) Methanol (Methyl Alcohol)

Advantages:
(A) a strong industrial solvent, excellent for animal and vegetable oils,
(B) low or no affinity for active carbon,
(C) good solubility for iodine,
(D) low cost,
(E) great ability to dissolve cigarette stains and smoke residues,
(F) miscible with water and other organic solvents.

Disadvantages:
(A) extremely low solubility for diesel fuel,
(B) flammable.

(16) Isopropanol (Isopropyl Alcohol)

Advantages:
(A) a strong solvent for petroleum hydrocarbons, resins, gums, alkaloids, shellac, and essential oils,
(B) miscible with water, diesel fuel, gasoline and organic solvents,
(C) ability to dissolve cigarette stains and smoke residues,
(D) good solubility for iodine,
(E) low cost.

Disadvantages:
(A) flammable.

(17) Freon 11 (Trichlorofluoromethane)

Advantages:
(A) an excellent organic solvent,
(B) nonflammable,
(C) low boiling point and low latent heat of vaporization for low energy recovery.

Disadvantages:
(A) ozone depletion,
(B) low solubility for water and iodine,
(C) incapable of dissolving cigarette stains,
(D) affinity for active carbon (residue or poisoning effect)
(E) boiling point is too close to common ambient temperature.

(18) Freon 21 (Dichlorofluoromethane)

Advantages:
(A) an excellent organic solvent,
(B) nonflammable,
(C) low boiling point and low latent heat of vaporization for ease of recovery.

(Con'd)

Table 13B. Summary of Advantages and Disadvantages, Potential Solvents Table 13A *(Con'd)*

(18) Freon 21 (Dichlorofluoromethane) *(Con'd)*

Disadvantage:

(A) boiling point is below common ambient temperature (usable only under pressure).

(19) Freon 113 (Trichlorotrifluoroethane)

Advantages:

(A) an excellent solvent and dry cleaning agent,
(B) nonflammable,
(C) low boiling point and low latent heat of vaporization for low energy recovery.

Disadvantages:

(A) ozone depletion,
(B) low solubility for water and iodine,
(C) incapable of dissolving cigarette stains,
(D) affinity for active carbon (residue or poisoning effect)

(20) Freon 114 (Dichlorotetrafluoroethane)

Advantages:

(A) an excellent solvent,
(B) nonflammable,
(C) lower affinity for active carbon than Freon 113.

Disadvantages:

(A) ozone depletion,
(B) boiling point is too low.

(21) Freon 114 B2 (Dibromotetrafluoroethane)

Advantages:

(A) an excellent solvent,

21) Freon 114 B2 (Dibromotetrafluoroethane)

Advantages: (Con'd)

(B) nonflammable,
(C) low boiling point and low latent heat of vaporization for low energy recovery.

Disadvantage:

(A) affinity for active carbon.

(22) Freon 132 (Dichlorodifluoroethane)

Advantages:

(A) an excellent solvent,
(B) non-flammable,
(C) low boiling point and low latent heat of vaporization for low energy recovery,
(D) a Freon solvent with no ozone impact,
(E) potentially lower affinity for active carbon than Freon 113.

Disadvantages:

(A) toxic (breathing Freon 132 contaminated air cause sterility in rats).

(23) Freon 123 (Dichlorotrifluoroethane)

Advantages:

(A) an excellent solvent, (superior to Freon 113),
(B) nonflammable,
(C) low boiling point for ease of recovery,
(D) a Freon solvent with no ozone impact,
(E) potentially lower affinity for active carbon than Freon 113.

Disadvantages:

(A) toxicity: 10 ppm

2. Solvent adsorption and retention on activated carbon

In the selection of an optimal solvent, emphasis was placed on the removal of diesel fuel contamination. There are numerous petroleum distillates which may be effective in dissolving and removing diesel fuel contaminants. However, these hydrocarbon solvents themselves may become new contaminants for the active carbon. Using gasoline as a solvent to facilitate the removal of diesel fuel is an example. Minimal solvent retention is an important consideration in the selection.

The affinity of active carbon for various selected solvents was determined by weight measurements. Because some solvents may affect the binder used in the manufacture of the foam material, loose granules of coconut shell activated carbon (Calgon PCB 12x30) were used. The carbon was dried in a 50°C vacuum oven, then weighed amounts in glass petri dishes were immersed in a solvent. After 10 minutes' soak, the solvents were allowed to evaporate in a fumehood for extended periods of time until the carbon granules became visibly dry. Further evaporation and desorption was continued by placing the petri dishes in a well ventilated room equipped with a large, high speed exhaust fan. After approximately 3 hours, glass covers were placed on the petri dishes and each carbon sample was separately dried in a 50°C vacuum oven for 30 minutes. Table 14 shows the retention for each solvent as per cent weight increase.

Table 14. Relative Affinity of Activated Carbon for Various Solvents

Solvent	Molecular Weight	Boiling Point °C	Weight of Carbon (g) initial	Weight of Carbon (g) evaporated	Weight of Carbon (g) 50°C, vac	Gain (%)
Acetone	58	56	2.2867	2.7816	2.4196	5.8
Benzene	78	80	2.0546	2.6314	2.3902	16
Bromobenzene	157	156	2.1458	3.4200	3.2619	52
Carbon Tetrachloride	154	77	2.2715	3.3820	3.0390	34
Methylene Chloride	85	40	2.0825	2.6032	2.1928	5.3
Perchloroethylene	166	121	2.1901	3.5570	3.2842	50
Trichloroethylene	131	87	2.0830	3.0642	2.7599	33
1,1,1, Trichloroethane	133	74	1.7857	2.4887	2.2148	24
Xylene	106	144	2.1086	2.8651	2.7487	30
Ethanol	46	78	2.4195	3.0449	2.5322	4.7
Methanol	32	65	2.1173	2.2868	2.1139	-0.16
Isopropanol	60	82	1.9855	2.5706	2.1566	8.6
Freon 113	187	48	1.8787	2.8594	2.3844	27
Gasoline			1.8999	2.5707	2.4933	31
Water	18	100	2.1140	2.7122	2.1118	-0.10

Only water and methanol were not adsorbed or retained by activated carbon in identical drying processes in a 50 °C vacuum oven for 30 minutes. Residual adsorption correlates roughly with the product of boiling point and molecular weight. For halogenated solvents, retention on activated carbon increases with the number of halogen atoms per molecule, and with the atomic weight of the halogen atom.

3. Solvent Power Evaluation: diesel fuel in three solvents

In the study to follow, Freon 113, isopropanol, and methanol were chosen for a more detailed evaluation. Freon 113 typifies various chlorinated and fluorinated hydrocarbon solvents and is also a popular specialty dry cleaning agent. Isopropanol represents a low cost, aliphatic hydrocarbon solvent and an alcohol. Methanol was chosen because of its unique property of not leaving any trace of residues on active carbon. Since there is no single scale to rate the solvent power on an absolute basis, attempt was made to determine the relative solubility of diesel fuel in the three selected solvents.

Type III carbon foam samples in 5 cm squares were used as test substrates. Samples were rinsed in distilled water to remove loose carbon. The weight of each test piece was determined after drying in a 50 °C vacuum oven. The various test samples were divided into two groups. The first group was subjected to diesel fuel contamination and subsequent solvent wash in an ultrasonic bath. The second control group, with no diesel contamination, was treated in an otherwise identical manner.

After soaking in diesel fuel for approximately 5 minutes, the test samples of the first group were blotted dry on lint-free tissue papers to remove excess contaminants. Loose and nonadsorbed diesel fuel within the carbon foam was further removed by rinsing in the respective solvent for one minute. The volume of solvent used was 100 mL in all cases. The test samples were then transferred separately to beakers each containing 250 mL of the respective solvent. After a 15 minute wash under ultrasonic excitation, the cleaning solvents were replaced and the process continued for an additional 15 minutes. The various test pieces were air dried in a fume hood and evacuated separately in a 50 °C vacuum oven for 30 minutes. After weighing, the 30 minute vacuum oven drying was repeated. The final weight was then recorded and the results are summarized in Table 15.

Table 15. A Comparison of Diesel Fuel Removal by Selected Solvents - Type III Foam Material

Solvent	Dry Wt g	Contaminant	30-minute Evacuation		60-minute Evacuation	
			Wt, g	Wt Gain %	Wt, g	Wt Gain %
Freon 113	0.6696	None	0.7176	7.2	0.7044	5.2
Freon 113	0.6650	Diesel Fuel	0.7185	8.1	0.7110	6.9
Isopropanol	0.7280	None	0.7332	0.71	0.7269	-0.15
Isopropanol	0.7183	Diesel Fuel	0.7533	4.9	0.7515	4.7
Methanol	0.6930	None	0.6804	-1.8	0.6799	-1.9
Methanol	0.7040	Diesel Fuel	0.7465	6.0	0.7463	6.0

The data in Table 15 confirm earlier test results (Table 14) that methanol is not retained by active carbon following a short duration of evacuation in a 50°C vacuum oven. However, isopropanol is also substantially removed after an evacuation period of 60 minutes, as opposed to the 30-minute duration used in the earlier tests on unbound carbon particles. The amount of diesel fuel retained by the carbon foam sample can be estimated and compared on a relative scale. Pertaining to each solvent, the diesel fuel retention based on data shown in Table 15 is:

Solvent	*Diesel Fuel Retention in % of carbon foam weight*	
Freon 113	6.9 % - 5.2 %	= 1.7 %
Isopropanol	4.7 % - (-0.15 %)	= 4.9 %
Methanol	6.0 % - (-1.9 %)	= 7.9 %

Among the selected solvents, Freon 113 appears to be the most effective for diesel fuel removal. Methanol, which has very low solubility for diesel fuel, is the least effective, as expected.

Despite pre-washing in distilled water, the Type III foam material is still somewhat susceptible to carbon loss. A different material, the Toyobo active carbon fiber fabric, was also used as a test substrate in an identical solvent-wash test. The corresponding results are summarized in Table 16.

Table 16. A Comparison of Diesel Fuel Removal by Selected Solvents - Toyobo Carbon Fiber Fabric

Solvent	g	Dry Wt Contaminant	30-minute Evacuation Wt, g	30-minute Evacuation Wt Gain %	60-minute Evacuation Wt, g	60-minute Evacuation Wt Gain %
Freon 113	0.8357	None	0.8873	6.2	0.8722	4.4
Freon 113	0.8659	Diesel Fuel	0.9266	7.0	0.9195	6.2
Isopropanol	0.8900	None	0.9022	0.14	0.8939	0.44
Isopropanol	0.8604	Diesel Fuel	0.9024	4.9	0.9007	4.7
Methanol	0.8779	None	0.8771	-0.091	0.8766	-0.15
Methanol	0.8294	Diesel Fuel	0.8550	6.7	0.8847	6.7

Solvent	*Diesel fuel retention in % of Toyobo AC fabric weight*	
Freon 113	6.2 % - 4.4 %	= 1.8 %
Isopropanol	4.7 % - 0.44 %	= 4.3 %
Methanol	6.7 % - (-0.15 %)	= 6.9 %

The above results with active carbon fiber fabric confirm the findings on Type III foam.

Although Freon 113 appears to be relatively efficient in reducing diesel fuel contamination, it will be shown in later presentations that it is not effective in restoring the sorptive power of contaminanted active carbon foam without the addition of iodine. Due to its low iodine solubility and high affinity for carbon, Freon 113 turns out not to be the solvent of choice after all.

B. IMPROVED APPARATUS FOR TESTING EXTENT OF REACTIVATION

1. A flow-controlled four-port apparatus with copper-flame detectors

More exacting vapor test control was desirable to assay the extent of cleaning on samples soiled with hydrocarbon-containing contaminants. A CCl_4 vapor test apparatus was built in which each station has individual challenge vapor flow controllers and propane torch/copper collar detectors. In the present study (Phase II-B), the simplified test apparatus was exclusively used in lieu of the standard method based on pyrolyzer/starch-iodide bubbler assay. Because the presence of residues of hydrocarbon contaminants and/or solvents is likely, especially in partially reactivated samples, the established method based on pyrolyzer/starch-iodide bubbler assay was abandoned. Dry air instead of nitrogen is used as the carrier gas in order to sustain a propane flame. The distinctive green flame characteristic of the presence of chlorine is not masked by the presence of residual contaminants or solvents.

Figure 12 shows a schematic diagram of the 4-station dynamic test apparatus used in the present study. A stream of dry air is bubbled through two CCl_4 vaporizers connected in series and maintained at 0°C. The cold effluent stream passes through a heat exchanger (copper tubing) and warms to ambient temperature (in a well-regulated, air-conditioned building). The CCl_4 partial pressure is constant, reproducible and equivalent to the equilibrium vapor pressure of CCl_4 at 0° C, as discussed in section V.A.2. The concentrated CCl_4 vapor stream is then diluted 10-fold by a second air stream, to form a challenging stream at 15 mg/L/min through each port.

The precise flow rates, essential for accurate measurement, are maintained by servo mass flow controllers. The correct settings for these flow controllers are determined and monitored via separate rotameters. Such a flow controller consists of a smooth-acting proportional electromagnetic servo valve, i.e., a voltage sensitive orifice, a PID (proportional integral and differential) automatic control circuit, and a flow sensor, as shown in Figure 13. The desired flow is controlled by the FLOW RATE SELECT potentiometer. Any deviations in the flow rate, detected by the flow sensor, will be amplified by the DIFFERENCE AMPLIFIER, and the resulting error signal is fed to the PID control circuit for appropriate correction and compensation by the servo valve. For convenience, indicator lights are installed to guard against possible errors and deviations in the actual flow rate.

In operation, the Dawson sample cup is connected downstream from the mixing flask (Figure 12). Initially, the carbon tetrachloride is completely adsorbed by the test specimen and only a blue flame appears above the copper plate of the propane halide detector. When the accumulated CCl_4 challenge finally reduces the adsorption rate, some CCl_4 molecules pass through the foam material and a faint green flame emerges within the blue flame. The elapsed time from the instant the sample cup is engaged to the flow until the moment when a tinge of green flame is first observed is recorded as the initial breaktime. When the test sample has finally adsorbed its full capacity, CCl_4 starts to penetrate at a higher rate so that a distinctive, large green flame appears, completely filling the space above the copper reaction plate. The elapsed time at this end point is recorded as the final breaktime.

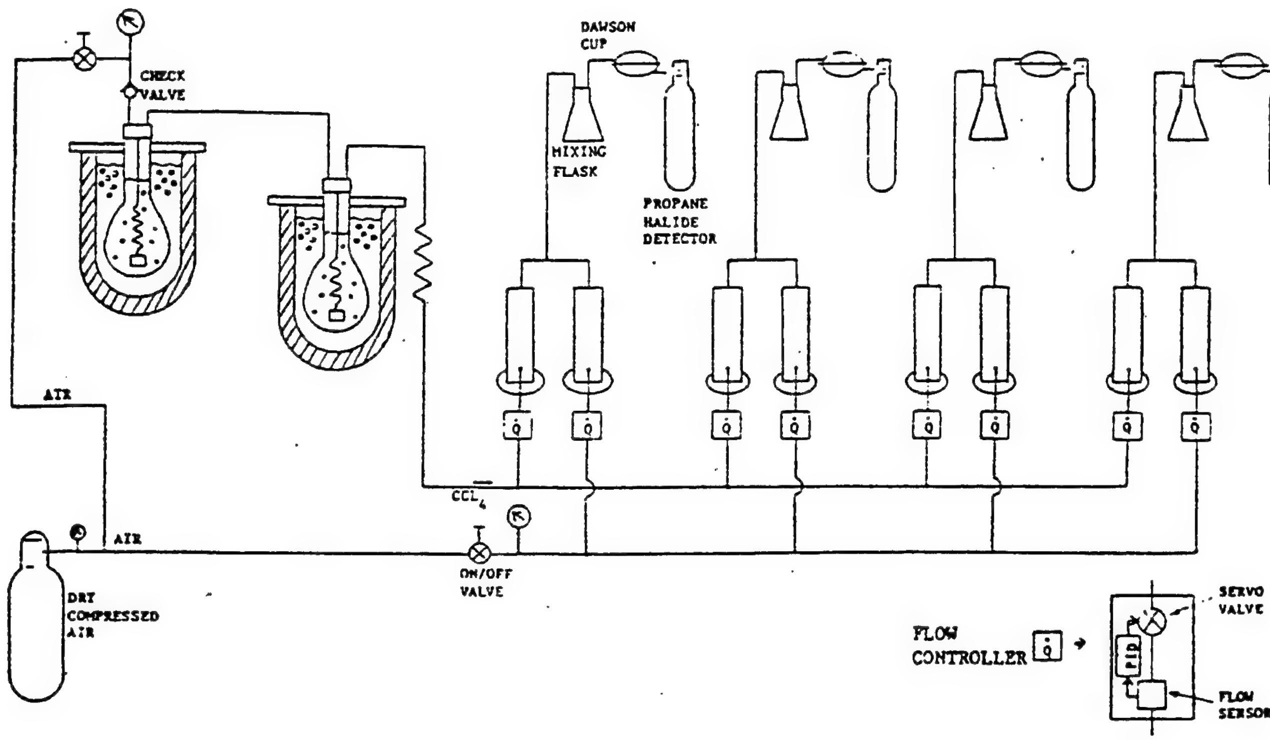


Figure 12. Schematic diagram of an improved four-station vapor penetration test apparatus with automatic flow control

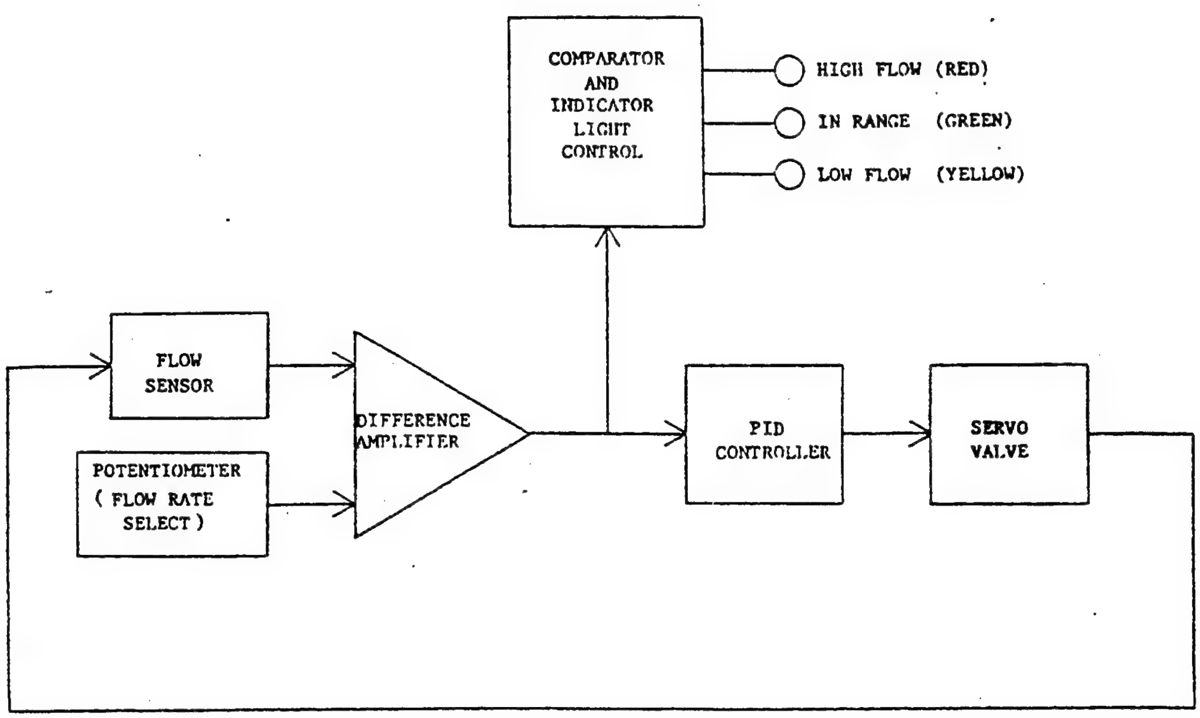


Figure 13. Diagrammatic representation of a closed loop flow controller

2. Effect of challenge concentration on dynamic sorption

For the dynamic test apparatus shown in Figure 12, the CCl_4 concentration can be varied by changing the mass flow rate of the vapor stream independently, keeping the carrier velocity at 10 cm/min (1 Lpm through the 100 sq cm sample). In order to assess the effect of concentration, uncontaminated fresh foam samples were tested at different CCl_4 mass flow rates and the results are summarized in Figure 14. It appears that the dynamic adsorption (breaktime x challenge rate) is insensitive to the CCl_4 vapor concentration above a threshold of approximately 4 mg/L. At challenge rates below 4 mg/L at 10 cm/min, the dynamic adsorption decreases with CCl_4 mass flow rate. The Type III foam material samples were preconditioned in a 50 °C vacuum oven before testing.

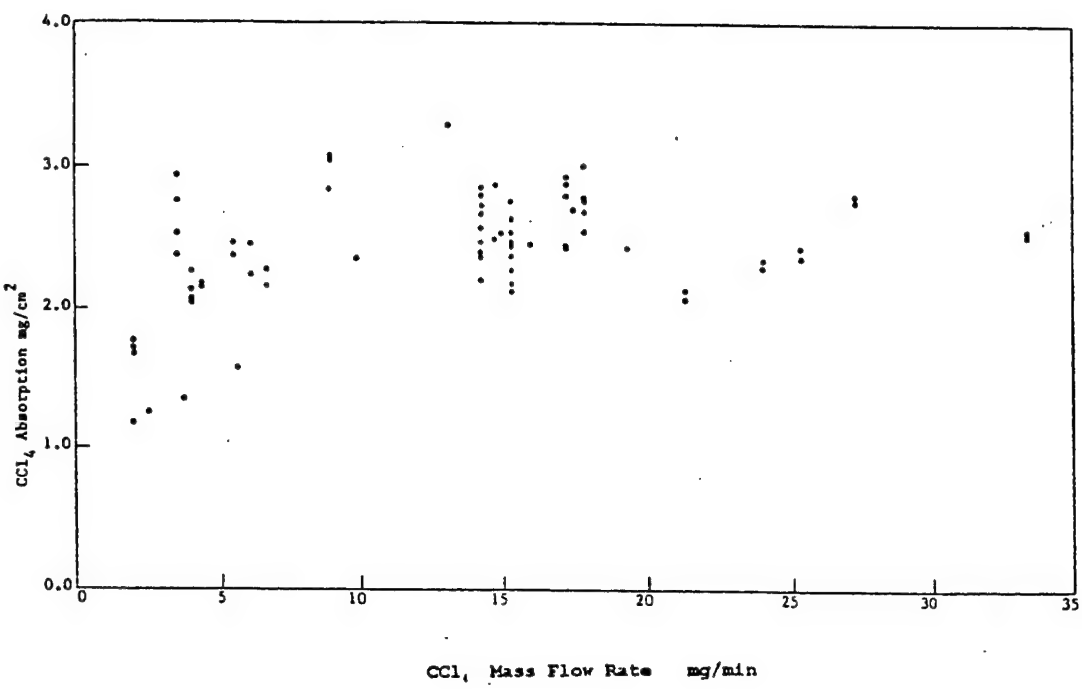


Figure 14. The effect of flow rate on adsorption

Finally, the efficacy of flame assay has been confirmed by repeated tests involving various contaminants and solvents used in the present study. Although the flame color may change in the presence of these species, it does not interfere or mask the distinctive green color of chlorine. For diesel fuel or gasoline soiled samples, the green flame appears within seconds, confirming the lack of sorptive power. As shown in Table 1, identically soiled samples give erroneous results when subjected to a standard dynamic absorption test involving the pyrolyzer/starch-iodide bubbler assay. A breakpoint was never observed during the three-hour test period due to interference of petroleum products.

Static CCl_4 adsorption tests are dynamic adsorption carried out to equilibrium, when samples attain constant weight. They are performed to assess the total capacity of treated samples.

C. SAMPLE TREATMENT

1. Reproducibility

To establish baseline performance, fresh Type III foam samples were evaluated in the dynamic CCl_4 adsorption test apparatus with copper-flame detector (Fig. 12). Before tests, samples were dried in a 50° C vacuum oven for at least two hours. Static tests, challenged until weight is constant to determine the maximum CCl_4 activity, are also reported. The test data are given in Table 17.

Table 17. Vapor Sorptivity of Uncontaminated Type III Foam Samples

Sample No	CCl_4 Vapor Adsorption Tests Dry Weight g	CCl_4 Flow mg/min	Dynamic Initial/Final mg/cm^2	Static Wt gain %
360	3.79	14.2	2.20/2.49	31.4
362	3.78	14.2	2.47/2.76	31.7
364	3.98	14.2	2.66/2.88	29.6
366	3.70	14.2	2.40/2.61	28.0
368	3.99	14.2	2.80/3.11	31.1
370	3.99	14.2	2.37/2.73	32.0
372	4.03	14.2	2.85/3.01	32.0
374	4.05	14.2	2.57/2.91	32.0
377	3.88	14.2	2.73/3.25	29.9
361	3.87	15.3	2.52/2.81	31.8
363	3.94	15.3	2.62/2.89	31.7
365	3.85	15.3	2.11/2.30	31.6
367	3.64	15.3	2.48/2.66	30.2
369	4.15	15.3	2.28/2.54	28.1
371	3.83	15.3	2.43/2.60	31.0
373	3.84	15.3	2.38/2.57	30.8
375	3.75	15.3	2.19/2.33	28.3
Mean Value			2.47/2.73	30.7
Standard Deviation			0.21/0.26	1.4

The above data indicate little correlation between sample weight and dynamic adsorption. Also, there does not appear to be good correlation between dynamic and static adsorption.

2. Effect of incomplete removal of solvent from sample on sorptivity

Of the possible nonaqueous solvents for further iodine displacement reactivation studies, Freon 113, isopropanol, and methanol, were chosen for a more detailed evaluation. Freon 113 typifies various chlorinated and fluorinated hydrocarbon solvents and is also a popular specialty dry cleaning agent. Isopropanol represents a low cost aliphatic hydrocarbon solvent and an alcohol. Methanol was chosen because of its unique property of not leaving any trace of residues on active carbon.

The effect of solvents on the sorptive power of Type III foam material was investigated. Fresh samples, initially subjected to a static (equilibrium) CCl_4 adsorption test, were subsequently washed in the selected solvents. After drying and evacuation in a 50° C vacuum oven for 30 minutes, the test samples were subjected to dynamic CCl_4 adsorption tests, and then challenged further in static tests to constant weight. Results are summarized in Table 18.

Table 18. Effect of Solvents on Sorptive Power of Active Carbon Foam

Sample No	Dry Wt, g	Initial Static CCl_4 Adsorption,g	Solvent	Wt Gain After Solvent Wash, g	Final Dynamic CCl_4 Adsorption mg/cm^2	Final Static CCl_4 Adsorption g
38	4.1773	5.2200	Freon 113	0.3322	1.80/1.97	5.2322
40	3.7815	4.6700	Methanol	-0.0931	2.89/3.33	4.6020
42	4.2498	5.3200	Isopropanol	0.0702	0.90/1.57	5.3145

The above results confirm the earlier finding that methanol is not retained by the active carbon. Compared to the fresh samples, dried two hours (Table 17), dynamic sorptive power is improved after methanol wash, perhaps due to removal of unknown contaminants originally existing on the carbon foam material. However the same gain was observed in later work, after microwave drying of methanol, but it disappeared on aging (Table 24), suggesting methanol retention in the impregnate binder enhances sorptivity just as water does. For Freon 113 and isopropanol, dynamic CCl_4 adsorptions were seemingly affected due to solvent retention in the carbon pores. It is interesting to note that, although solvent retention was worse with sample 38 than 42 (as evidenced from the weight gain after solvent wash), the dynamic adsorption for sample 38 was actually much higher. One possible explanation is that CCl_4 molecules were acting, during the dynamic test, as a displacing agent which happened to favor the desorption of Freon 113 over isopropanol.

3. Experimental Protocol

Three kinds of Type III AC/foam, according to stages of treatment, were to be analyzed: uncontaminated, contaminated, and reactivated samples.

The density and sorptive power of the current type III foam material is not particularly uniform and there is a significant data scattering in terms of the dynamic CCl_4 absorption. This dynamic adsorption does not appear

to correlate well with either the weight or the optical transparency of the test sample. Therefore, the sorptive power of test samples needs to be established individually. The following protocol was adopted:

(1) Die cut foam material to five-inch diameter for mounting in a Dawson cup

(2) Store test samples in a 50° C vacuum oven for at least two hours to remove water vapor and other volatile species accumulated in storage

(3) Record sample weight after each piece is subjected to gentle vibration, bouncing, shaking and tapping to remove loose carbon particles

(4) Perform initial dynamic CCl_4 adsorption tests to document the sorptive power before contamination and reactivation

(5) Conduct initial static CCl_4 adsorption tests to record the CCl_4 activity prior to contamination and reactivation

(6) De-gas samples in a 50° C vacuum oven until there is no significant drop in vacuum pressure

(7) Contaminate samples

(8) Reactivate samples (drying procedures, see below)

(9) Store samples in a 50° C vacuum oven for at least two hours prior to testing

(10) Record sample weight after reactivation

(11) Obtain dynamic CCl_4 adsorption data of reactivated samples

(12) Record static CCl_4 adsorption data of reactivated samples

Prior to testing, the various types of specimens were dried as follows:

(1) Uncontaminated samples - pre-conditioned in a 50 ° C vacuum oven for at least two hours,

(2) Contaminated samples - hanged dry in a fume hood and then preconditioned in a 50 °C vented oven overnight,

(3) Reactivated samples -
   a. partially processed or fully reactivated - 50 ° C vacuum oven ≥ two hours
   b. fully reactivated - microwave-vacuum oven

4. Controlled contamination

Various selected contaminants were separately applied to the test material in a controlled, reproducible

manner. In order to assess the true efficacy of the reactivation process, efforts were made to apply each contaminant to the utmost extent, that is, in a manner far more severe than expected in real life, to ensure maximum coverage, full penetration, and complete saturation by the contaminant.

The various contaminants tested, and controlled application methods, were previously described in section 3, (1) through (12).

D. FASTER REACTIVATION IN ULTRASONIC BATHS

1. Cleaning Apparatus

In Phase II-B the current chemical protective material, Type III activated carbon-impregnated foam, is used as a test substrate. Because carbon particles are adhesively bonded to the polyurethane foam, a nonagitative cleaning action is required in order to minimize carbon loss.

For cleaning in an organic solvent, the conventional agitative method for laundering in water was replaced by a milder means of solvent sweeping. The cleaning fluid or solvent was made to pass gently over the foam material. Contaminants which desorbed from the various micro- and macropores were removed when they slowly migrated into the fluid stream. Although this method is workable, it was found to be somewhat inefficient, time consuming, and required a large volume of cleaning fluid. In the present study, the solvent sweep technique is assisted by ultrasonic excitation.

If the apparatus for the above mentioned solvent sweep technique is immersed in an ultrasonic tank filled with water, the ultrasonic energy coupled through water will create high frequency alternating high and low pressure waves in the solvent. This action forms microscopic bubbles that expand and form cavities during the low pressure cycle, and implode and collapse at the high pressure cycle. The result is mechanical scrubbing on a scale that induces microscopic solvent movement within micropores. For a typical 55 KHz ultrasonic bath, the microscrubbing action is repeated 55,000 times per second, extending throughout the entire solvent space.

The Type III foam material was subjected to repeated ultrasonic excitation in water as well as in solvents (Freon 113, isopropanol, methanol, etc.) over extended test periods. There was no additional carbon loss, which is attributable to the ultrasonic action based on actual weight measurements with and without ultrasound under identical reactivation conditions. The fluid appeared to mix well so that sweeping a flow of solvent becomes unnecessary. Test samples, 5 inch diameter, were immersed and reactivated in solvents contained in wide mouth Pyrex glass jars, 6 inch diameter, 7.5 inch deep and 1/16 inch thick. These jars, equipped with screw-on covers, were in turn immersed in an ultrasonic bath with the following specifications:

Manufacturer: Branson Cleaning Equipment Company, Shelton, CT
Model: Branson B-92H
Tank Dimension: 50 cm L x 29 cm W x 20 cm D (8 gal.)
Power: 830 Watts
Frequency: 55 KHz

2. The ultrasonic cleaning process

Prior to regeneration, diesel fuel and gasoline soaked samples were pre-rinsed in the specific solvent selected for the reactivation, to remove excess amounts of contaminants. Pre-rinsing was not required for other contaminant types.

The ultrasonic solvent regeneration process is separated into four 15-minute periods. At the end of each period, the ultrasound is switched off and the outer water bath is drained and then refilled with fresh tap water to limit the temperature rise. Similarly, the solvent within the Pyrex glass jar containing the test sample is also replaced with a new supply of fresh, clean solvent. At the end of the final regeneration step, the test sample is placed on blotting papers to remove excess solvents. The test sample is then transferred to a vacuum oven maintained at 50 °C or a microwave vacuum oven. The volume of solvent used is approximately 500 mL per sample per period.

Solvent regenerations of AC/foam samples were conducted both with and without iodine. For those cases where iodine was used, the iodine crystals were added directly to the solvent to a concentration of approximately 8 g/L. For some solvents such as Freon 113, 1 g/L was used and still only a small portion of the iodine added actually dissolved in the solvent.

Sodium thiosulfate solution at a concentration range of 0.01 N to 0.1 N was found to be effective for complete removal of adsorbed iodine. The choice of sodium thiosulfate over other reducing agents is based on its exceptionally low cost advantage. Water rinse removes NaI, $Na_2S_4O_6$ and excess unreacted $Na_2S_2O_3$.

E. RESULTS: Three replicates x five soils x three solvents x five steps of reactivation

1. CCl_4 tests

For dynamic tests, the test system (Figure 12) was allowed to equilibrate for at least one hour after initiation of air flow. The CCl_4 flow rate was then determined using active-carbon-filled Schwartz U-tubes. For each test station, four separate calibration runs were performed with two consecutive runs in the morning before the vapor penetration study and two in the afternoon at the conclusion of the last test. For each test station, the CCl_4 flow calibrations were generally well within 3 % of each other throughout the day. The daily average value was then used in the calculation of CCl_4 adsorption. The sample cells were standard Dawson cups from Natick Labs; the effective surface area of each test specimen was taken to be 100 cm^2, nominally.

For static tests, the specimen weight was recorded at different stages of the pre-conditioning, reactivation and testing sequence. These weight measurements are designated as follows:

- W0 - initial (dry) weight
- W1 - initial static CCl_4 adsorption weight
- W2 - specimen weight after reactivation
- W3 - final equilibrium CCl_4 adsorption weight

Therefore, the following useful parameters can be defined

Initial CCl_4 adsorption activity (in % of dry sample weight):

$$\alpha = (W_1 - W_0)\, x \frac{100}{W_0}$$

Weight gain or loss, as a combined result of static CCl_4 adsorption test, contamination and reactivation:

$$\beta = (W_2 - W_0)\, x \frac{100}{W_0}$$

Final CCl_4 adsorption activity (in % of reactivated sample weight):

$$\gamma = (W_3 - W_2)\, x \frac{100}{W_2}$$

It should be noted that W_2, the reactivated sample weight, may not be equal to W_0, the initial sample weight due to the following factors:

(1) carbon loss - loose, unbound active carbon particles may separate from the foam sample in the solvent wash process,

(2) CCl_4 residue - as a result of the initial dynamic and static test,

(3) contaminant residue - in cases when the reactivation process is not complete,

(4) solvent retention - in cases when the solvent is not completely removed in the final drying and preconditioning stages,

(5) other residues - such as iodine, sodium thiosulfate and impurities in solvent and rinsing water.

2. Steps of reactivation

In order to elucidate the reactivation mechanism, contaminated samples were subjected to partial as well as complete reactivation steps. The various levels of regeneration are:

(1) Organic solvent wash - identified by F113, ISO and MET for Freon 113, isopropanol and methanol, respectively.

Contaminated samples were washed in the selected organic solvent with the aid of ultrasonic excitation.

(2) Iodine/organic solvent wash (aqueous thiosulfate rinse), - identified by I/F113, I/ISO and I/MET for the three selected solvents, Freon 113, isopropanol and methanol, respectively.

Iodine was added to the solvent as a displacement agent to facilitate the removal of contaminant. The iodine concentrations used were 1 g/l for Freon 113, 8 g/l for isopropanol and methanol. At room temperature, the iodine solubility in Freon 113 is less than 1 g/l and not all iodine crystals were dissolved in the solvent until some iodine molecules were adsorbed on the active carbon.

(3) Iodine/organic solvent wash (aqueous thiosulfate rinse), followed by methanol rinse - identified by I/F113 & MET and I/ISO & MET, respectively.

After iodine/solvent wash, the test sample was rinsed in methanol to remove solvent residue. Because methanol has a very low affinity for active carbon, it was completely removed in the final drying process.

(4) Iodine/organic solvent wash (aqueous thiosulfate rinse), plus methanol rinse and followed by microwave drying - identified by "I/F113 & MET & μW" and "I/ISO & MET &μW", respectively, for Freon 113 and isopropanol.

Instead of drying in a 50 °C vacuum oven, reactivated samples were dried in a vacuum chamber placed inside a high power microwave oven.

3. Diesel Fuel Contamination

For diesel fuel contaminated active carbon foam material, the goal of complete reactivation has been achieved. Full recovery of the sorptive power was possible with an iodine-assisted, solvent-wash process. Both static and dynamic CCl_4 adsorption capabilities were restored following contamination and subsequent reactivation.

The experimental data corresponding to different levels of reactivation are given in Table 19.

Table 19. Performance of Reactivated Samples Contaminated by Diesel Fuel

Table 19A. *Static Test Results*

Sample No	Weight in Grams W0	W1	W2	W3	Reactivation Process	Weight Change in % α	β	γ
198	3.9872	5.2113	-	*	None	30.7	-	*
199	4.0215	5.2231	-	*	None	29.9	-	*
230	3.9625	*	-	*	None	*	-	*
231	3.9991	*	-	*	None	*	-	*
325	4.1620	5.3800	4.3951	5.3608	F113	29.3	5.6	22.0
326	4.0744	5.2720	4.2740	5.3899	F113	29.4	4.9	26.1
327	4.0795	5.2910	4.2104	5.1135	F113	29.7	3.2	21.4
328	4.1942	5.4515	4.2907	5.3248	F113	30.0	2.3	24.1
329	4.1400	5.3700	4.2872	5.1680	ISO	29.7	3.6	20.5
330	4.0079	5.1400	4.2127	5.1606	ISO	28.2	5.1	22.5
331	4.0125	5.1682	4.2088	5.0169	ISO	28.8	4.9	19.2
332	4.1022	5.3418	4.3315	5.1826	ISO	30.2	5.6	19.7
333	3.9821	5.2265	4.2652	5.0294	MET	31.3	7.1	17.9
334	3.9966	5.2018	4.3083	5.0492	MET	30.2	7.8	17.2
335	4.1028	5.3154	4.3879	5.1878	MET	29.6	7.0	18.2
336	4.0626	5.2322	4.3862	5.1144	MET	28.8	8.0	16.6
360	3.7900	4.9800	3.7902	4.5790	I/F113	31.4	0.	20.8
361	3.8700	5.1000	3.8668	4.7220	I/F113	31.8	-0.1	22.1
362	3.7880	4.9900	3.7820	4.6900	I/F113	31.7	-0.2	24.0
363	3.9400	5.1900	3.9074	4.7300	I/F113	31.7	-0.8	21.1
364	3.9830	5.1600	3.8278	4.7620	I/ISO	29.6	-3.9	24.4
365	3.8500	5.0650	3.5968	4.4400	I/ISO	31.6	-6.6	23.4
366	3.7000	4.7350	3.5224	4.3960	I/ISO	28.0	-4.8	24.8
367	3.6450	4.7450	3.4664	4.3100	I/ISO	30.2	-4.9	24.3
356	3.9600	5.0850	3.9106	4.5170	I/MET	28.4	-1.2	15.5
357	3.9040	5.0150	3.8346	4.4560	I/MET	28.5	-1.8	16.2
358	3.6830	4.6500	3.3588	3.8700	I/MET	26.3	-0.9	15.2
359	3.9800	5.0650	3.9561	4.6150	I/MET	27.3	-0.6	16.7
170	3.7207	4.5100	3.5000	4.2000	I/F113 & MET	21.2	-5.9	20.0
171	4.3105	5.3700	4.1900	4.9000	I/F113 & MET	24.6	-2.8	17.0
218	4.1825	5.2436	4.0105	4.8543	I/F113 & MET	25.4	-4.1	21.0
219	4.2676	5.2466	4.1525	5.0621	I/F113 & MET	22.9	-2.7	21.9
172	4.2103	5.3000	3.9000	4.8700	I/ISO & MET	25.9	-7.4	24.9
173	4.2107	5.3100	3.9638	4.9000	I/ISO & MET	26.1	-5.9	23.6
220	3.9849	4.9565	3.6744	4.5796	I/ISO & MET	24.4	-7.8	24.6
223	4.1148	5.1100	3.8795	4.8377	I/ISO & MET	24.2	-5.7	24.7
372	4.0340	5.3250	3.6890	4.8530	I/ISO & MET	32.0	-8.6	31.6
373	3.8470	5.0300	3.6110	4.7380	I/ISO & MET	30.8	-6.1	31.2
374	4.0550	5.3500	3.7534	4.9430	I/ISO & MET	32.0	-7.4	31.7
375	3.7520	4.8150	3.5479	4.5560	I/ISO & MET	28.3	-5.4	28.4
376	3.8550	4.9950	3.6021	4.7620	I/ISO & MET & uW	29.6	-6.6	32.2
377	3.8870	5.0500	3.7008	4.8880	I/ISO & MET & uW	29.9	-4.8	32.1
378	3.8580	5.0500	3.6188	4.7880	I/ISO & MET & uW	30.9	-6.2	32.3
379	4.0330	5.3100	3.7144	4.9330	I/ISO & MET & uW	31.7	-7.9	32.8

* CCl_4 absorption test omitted.

Table 19B. Dynamic Test Results

	Uncontaminated			Contaminated and Reactivated	
Sample No	CCl_4 Flow mg/min	Dynamic Absorption Initial/Final mg/cm^2	Reactivation Process	CCl_4 Flow mg/min	Dynamic Absorption Initial/Final mg/cm^2
198	14.3	2.60/2.83	NONE	15.3	0/0.01
199	14.3	2.55/2.73	NONE	15.3	0/0.01
230	*	*	NONE	15.3	0.01/0.01
231	*	*	NONE	15.3	0.01/0.01
325	17.2	2.89/3.27	F113	15.1	0.21/0.40
326	17.8	2.76/3.01	F113	15.1	0.32/0.44
327	17.2	2.80/3.20	F113	15.1	0.17/0.29
328	17.8	3.01/3.38	F113	15.1	0.22/0.35
329	17.2	2.91/3.27	ISO	15.0	0.20/0.30
330	17.8	2.56/2.76	ISO	15.0	0.31/0.46
331	14.7	2.49/2.72	ISO	15.0	0.18/0.29
332	14.7	2.60/2.79	ISO	15.0	0.22/0.33
333	15.2	2.71/2.88	MET	15.3	0.60/0.78
334	15.2	2.44/2.62	MET	15.3	0.52/0.77
335	15.2	2.48/2.60	MET	15.3	0.54/0.74
336	15.2	2.39/2.66	MET	15.3	0.50/0.82
360	14.2	2.20/2.49	I/F113	15.2	1.66/1.78
361	15.3	2.52/2.81	I/F113	15.2	1.92/2.08
362	14.2	2.47/2.76	I/F113	15.2	1.94/2.24
363	15.3	2.62/2.89	I/F113	15.2	1.93/2.29
364	14.2	2.66/2.88	I/ISO	15.1	2.24/2.48
365	15.3	2.11/2.30	I/ISO	15.1	1.78/1.99
366	14.2	2.40/2.61	I/ISO	15.1	2.00/2.24
367	15.3	2.48/2.66	I/ISO	15.1	2.02/2.28
356	17.2	2.44/2.68	I/MET	15.3	1.47/1.68
357	17.8	2.69/2.87	I/MET	15.3	1.55/1.74
358	17.2	2.41/2.63	I/MET	15.3	1.47/1.66
359	17.8	2.79/2.99	I/MET	15.3	1.58/1.80
170	13.1	2.82/3.00	I/F113 & MET	14.8	1.63/1.77
171	13.1	2.63/2.88	I/F113 & MET	12.2	1.95/2.07
218	13.8	2.75/3.28	I/F113 & MET	13.4	2.13/2.27
219	13.8	2.95/3.42	I/F113 & MET	13.6	2.31/2.44
172	13.7	2.67/3.07	I/ISO & MET	13.4	2.44/2.60
173	13.7	2.74/2.95	I/ISO & MET	14.8	2.51/2.66
220	13.4	2.83/3.24	I/ISO & MET	13.6	2.65/2.78
223	13.4	2.87/3.36	I/ISO & MET	12.2	2.62/2.74
372	14.2	2.85/3.01	I/ISO & MET	15.2	2.70/2.94
373	15.3	2.38/2.57	I/ISO & MET	15.2	2.22/2.50
374	14.2	2.57/2.91	I/ISO & MET	15.2	2.45/2.82
375	15.3	2.19/2.33	I/ISO & MET	15.2	2.24/2.48
376	16.0	2.47/2.66	I/ISO & MET & uW	15.0	2.20/2.56
377	14.2	2.73/3.25	I/ISO & MET & uW	15.0	2.54/2.96
378	14.9	2.52/2.97	I/ISO & MET & uW	15.0	2.41/2.86
379	14.7	2.50/3.07	I/ISO & MET & uW	15.0	2.48/2.76

* CCl_4 absorption test omitted.

Based on the data presented in Table 19, the following conclusions can be drawn:

(1) Solvent wash alone without the benefit of iodine is not effective in restoring the sorptive power. In addition to the serious deficiency in contaminant removal, solvent adsorption on active carbon is a major contributing factor. This is evident from the observation that methanol which is readily desorbable from active carbon actually gave a better performance than either Freon 113 or isopropanol even though diesel fuel is insoluble in methanol whereas it is miscible with both Freon 113 and isopropanol.

(2) With the use of iodine as a displacing agent, the sorptive power recovery is dramatically enhanced.

(3) With the addition of an extra methanol rinse cycle to eliminate solvent adsorption, the sorptive power recovery is further improved especially in the case of iodine/isopropanol wash plus methanol rinse. Freon 113 is not as effective perhaps due to its low solubility for iodine.

(4) Although the dynamic adsorption was 5-9% lower after regeneration for test samples 172, 173, 220, 223, 372 through 374, Table 19B, the reactivation should be regarded as being "complete" due to 6-9% weight loss for these samples, Table 19A.

(5) 50°C/vacuum/microwave drying of methanol-rinsed samples of impregnated foam does not enhance sorptive power.

4. Gasoline contamination

The performance of reactivated samples contaminated by gasoline is summarized in Table 20.

Table 20. Performance of Reactivated Samples Contaminated by Gasoline

Table 20A. *Static Test Results*

Sample No.	Weight in Grams W0	W1	W2	W3	Reactivation Process	Weight Change in % α	β	γ
194	3.8633	*	-	*	None	*	-	*
195	3.8425	4.9420	-	*	None	28.6	-	*
196	3.9283	5.1160	-	*	None	30.2	-	*
197	3.9800	5.1630	-	*	None	29.7	-	*
44	3.9699	4.9000	4.3318	4.8755	F113	23.4	9.12	12.6
86	3.6134	4.4700	3.8420	4.4300	F113	23.7	6.3	15.3
87	3.6513	4.5150	3.9000	4.5300	F113	23.7	6.8	16.2
88	4.2000	5.2800	4.5008	5.3050	F113	25.7	7.2	17.9
55	3.8800	4.7920	4.1920	4.7727	ISO	23.5	8.04	13.6
89	4.2402	5.3500	4.2019	4.9900	ISO	26.2	-0.5	18.8
90	3.9683	4.9500	3.9120	4.6500	ISO	24.7	-1.4	18.9
91	4.1040	5.2200	4.0713	5.1000	ISO	27.2	-0.8	25.3
46	4.2833	5.3600	4.3382	5.2363	MET	25.1	1.28	20.7
43	4.3642	5.4500	4.2694	5.0900	I/F113	24.9	-2.2	19.2
47	3.6617	4.4716	3.5061	4.2134	I/ISO	22.1	-4.3	20.2
140	4.0820	5.1800	3.7990	4.6900	I/ISO	26.9	-6.9	23.5
141	4.0281	5.0500	3.8666	4.7800	I/ISO	25.4	-4.1	23.6
142	4.0625	5.1800	3.7495	4.5350	I/ISO	27.5	-7.7	21.0
45	4.0386	5.0000	3.8866	4.6860	I/MET	23.6	-3.8	20.6
368	3.9900	5.2300	3.7945	4.9790	I/ISO & MET	31.1	-4.9	31.2
369	4.1500	5.3150	3.9478	5.1800	I/ISO & MET	28.1	-4.9	31.2
370	3.9950	5.2750	3.8205	5.0400	I/ISO & MET	32.0	-4.4	31.9
371	3.8330	5.0200	3.6111	4.7470	I/ISO & MET	31.0	-5.8	31.5
380	4.1600	5.4450	3.9158	5.1730	I/ISO & MET& uW	30.9	-5.9	32.1
381	3.9323	5.0590	3.6905	4.8690	I/ISO & MET& uW	28.7	-6.2	31.9

* CCl_4 adsorption test omitted.

Table 20B. Dynamic Test Results

	Uncontaminated		Contaminated and Reactivated		
Sample No	CCl_4 Flow mg/min	Dynamic Adsorption Initial/Final mg/cm^2	Reactivation Process	CCl_4 Flow mg/min	Dynamic Adsorption Initial/Final mg/cm^2
194	*	*	NONE	14.9	0.04/0.05
195	16.3	2.53/2.71	NONE	14.9	0.04/0.05
196	17.5	2.70/2.92	NONE	14.9	0.03/0.04
197	14.7	2.87/3.05	NONE	14.9	0.05/0.06
44	*	*	F113	14.0	0.34/0.56
86	*	*	F113	16.1	0.27/0.42
87	*	*	F113	15.7	0.24/0.33
88	*	*	F113	15.7	0.25/0.39
55	*	*	ISO	14.0	1.44/1.81
89	*	*	ISO	16.1	0.52/0.71
90	*	*	ISO	16.1	0.45/0.64
91	*	*	ISO	13.2	0.53/0.86
46	*	*	MET	14.0	2.84/3.33
43	*	*	I/ F113	14.0	2.38/3.01
47	*	*	I/ ISO	14.0	2.31/2.87
140	*	*	I/ ISO	16.3	2.61/2.80
141	*	*	I/ ISO	16.1	2.56/2.71
142	*	*	I/ ISO	16.1	2.25/2.37
45	*	*	I/ MET	14.0	2.70/3.18
368	14.2	2.80/3.11	I/ ISO&MET	15.0	2.59/2.94
369	15.3	2.28/2.54	I/ ISO&MET	15.0	2.26/2.56
370	14.2	2.37/2.73	I/ ISO&MET	15.0	2.28/2.66
371	15.3	2.43/2.60	I/ ISO&MET	15.0	2.33/2.68
380	15.4	2.77/3.08	I/ ISO&MET&uW	15.0	2.67/3.05
381	15.1	2.33/2.64	I/ ISO&MET&uW	15.0	2.30/2.62

* CCl_4 adsorption test omitted.

Based on the data presented in Table 20, the following observations can be made:

(1) Solvent wash alone without the benefit of iodine is not effective (with the exception of methanol which is miscible with gasoline and is not retained by active carbon),

(2) With iodine, the sorptive power recovery is greatly enhanced,

(3) As in the case of diesel fuel contamination, complete recovery of the sorptive power is obtained with samples washed in iodine/isopropanol and rinsed in methanol. The same is also true for samples oven-dried in a microwave field, but there is no enhancement of sorptivity.

5. Cigarette smoke contamination

The performance of reactivated samples contaminated with cigarette smoke deposits is summarized in Table 21.

Table 21. Performance of Reactivated Samples Contaminated by Cigarette Smoke Deposits

Table 21A. *Static Test Results*

Sample No	Weight in Grams W0	W1	W2	W3	Reactivation Process	Weight Change in % α	β	γ
83	3.8910	4.8500	-	-	None	24.7	-	-
84	3.9940	5.0000	-	-	None	25.2	-	-
85	3.8547	4.8075	-	-	None	24.7	-	-
211	4.2155	*	-	-	None	*	-	30.0
212	4.2900	*	-	-	None	*	-	30.5
213	4.2638	*	-	-	None	*	-	29.8
214	4.0060	*	-	-	None	*	-	29.1
174	4.1226	5.2200	3.7775	4.9900	I/ISO	26.6	-8.4	32.1
175	3.5930	4.4800	3.3144	4.2300	I/ISO	24.7	-7.8	27.6
176	3.6426	4.5500	3.3902	4.4400	I/ISO	24.9	-6.9	31.0
177	4.3350	5.5000	4.1299	5.3300	I/ISO & uW	26.9	-4.7	29.1
382	4.3120	5.4700	4.1499	5.4160	I/ISO & MET	26.9	-3.8	30.5
383	4.2625	5.4100	4.0895	5.3000	I/ISO & MET	26.9	-4.1	29.6
384	4.0005	5.0600	3.8495	5.0520	I/ISO & MET& uW	26.5	-3.8	31.2
385	3.9341	4.9500	3.7795	4.9310	I/ISO & MET& uW	25.8	-3.9	30.5

Table 21B. *Dynamic Test Results*

	Uncontaminated		Contaminated and Reactivated		
Sample No	CCl_4 Flow mg/min	Dynamic Adsorption Initial/Final mg/cm^2	Reactivation Process	CCl_4 Flow mg/min	Dynamic Adsorption Initial/Final mg/cm^2
83	*	-	NONE	16.3	0.10/0.16
84	*	-	NONE	17.5	0.07/0.16
85	*	-	NONE	14.7	0.06/0.12
211	*	-	NONE	13.3	2.29/2.50
212	*	-	NONE	13.3	2.58/2.83
213	*	-	NONE	13.3	2.04/2.18
214	*	-	NONE	13.3	2.34/2.54
174	*	-	I/ ISO	14.7	2.78/3.04
175	*	-	I/ ISO	17.5	2.38/2.73
176	*	-	I/ ISO	16.3	2.53/2.74
177	*	-	I/ ISO & uW	13.6	2.98/3.26
382	14.9	2.67/2.98	I/ ISO & MET	15.0	2.64/2.89
383	14.9	2.62/2.96	I/ ISO & MET	15.0	2.66/2.90
384	14.9	2.48/2.68	I/ ISO & MET & uW	15.0	2.65/2.86
385	14.9	2.51/2.80	I/ ISO & MET & uW	15.0	2.48/2.74

* CCl_4 adsorption test omitted.

Based on data presented in Table 21, the following observations can be made:

(1) Because the test protocol of the present study calls for a measurement of the CCl_4 absorption prior to contamination and reactivation, CCl_4 retention persisted despite prolonged periods of vacuum evacuation at 50 °C. Samples 83, 84 and 85, although similarly contaminated, have far inferior sorptive power than that of samples 211, 212, 213 and 214 which were not subjected to a CCl_4 absorption test beforehand.

(2) Based on the dynamic adsorption data of samples 211 through 214, cigarette smoke contamination does not appear to have a significant effect on the CCl_4 sorptive power of active carbon.

(3) As in cases involving diesel fuel and gasoline contamination, complete recovery of the sorptive power is obtained in cases involving iodine/isopropanol wash plus methanol rinse, and with no additional activity after microwave drying.

6. Engine exhaust contamination

The performance of reactivated samples contaminated with gasoline engine exhaust is summarized in Table 22.

Table 22. Performance of Reactivated Samples Contaminated with Engine Exhaust

Table 22A. *Static Test Results*

Sample No	Weight in Grams W0	W1	W2	W3	Reactivation Process	Weight Change in % α	β	γ
118	4.1290	5.3600	-	5.3000	None	29.8	-	28.4
119	4.1356	5.3300	-	5.2000	None	28.9	-	25.7
120	4.1300	5.2350	-	5.1800	None	26.8	-	25.4
201	3.8620	*	-	4.9500	None	*	-	28.2
202	3.8935	*	-	5.0150	None	*	-	28.8
203	3.9947	*	-	5.0100	None	*	-	25.4
204	3.7685	*	-	4.6800	None	*	-	24.2
109	3.9375	5.0900	3.6458	4.7950	I/ ISO	29.3	-7.4	31.5
110	4.0062	5.2100	3.7783	4.9225	I/ ISO	30.1	-5.7	30.3
111	4.0465	5.2500	3.8975	5.0100	I/ ISO	29.7	-3.7	28.5
390	4.0879	5.3700	3.9699	5.2230	I/ ISO & MET	31.4	-2.9	31.6
391	4.1551	5.4600	4.0272	5.3030	I/ ISO & MET	31.4	-3.1	31.7
392	4.1367	5.3700	3.9737	5.2160	I/ ISO & MET & uW	29.8	-3.9	31.3
393	3.6200	4.6400	3.4450	4.5520	I/ ISO & MET & uW	28.2	-4.8	32.1

*CCl_4 adsorption test omitted.

Table 22B. Dynamic Test Results

	Uncontaminated			Contaminated and Reactivated	
Sample No	CCl_4 Flow mg/min	Dynamic Adsorption Initial/Final mg/cm^2	Reactivation Process	CCl_4 Flow mg/min	Dynamic Adsorption Initial/Final mg/cm^2
118	*	*	NONE	16.3	0.05/0.07
119	*	*	NONE	17.5	0.04/0.05
120	*	*	NONE	14.7	0.01/0.04
201	*	*	NONE	13.3	2.05/2.22
202	*	*	NONE	13.6	2.29/2.50
203	*	*	NONE	13.3	2.18/2.42
204	*	*	NONE	13.6	2.01/2.18
109	*	*	I/ ISO	16.3	2.77/3.16
110	*	*	I/ ISO	14.7	2.97/3.15
111	*	*	I/ ISO	17.5	2.77/2.89
390	15.0	2.43/2.65	I/ ISO & MET	14.9	2.66/2.88
391	15.0	2.46/2.65	I/ ISO & MET	14.9	2.74/2.93
392	15.0	2.44/2.70	I/ ISO & MET & uW	14.9	2.56/2.78
393	15.0	2.35/2.58	I/ ISO & MET & uW	14.9	2.44/2.64

* CCl_4 adsorption test omitted.

Based on data presented in Table 22, the following observations can be made:

(1) Samples 118, 119 and 120 have very low dynamic absorption due to CCl_4 retention from the static CCl_4 absorption test performed prior to contamination.

(2) Engine exhaust unmistakably has some detrimental effect on the sorptive power of carbon foam, as evident from the somewhat lower dynamic adsorption of samples 201 through 204.

(3) Complete recovery of sorptive power was obtained with iodine/ isopropanol wash plus methanol rinse, with or without microwave drying.

7. Simulated human sweat contamination

The performance of reactivated samples subjected to simulated human sweat contamination is summarized in Table 23.

Table 23. Performance of Reactivated Samples Contaminated with Simulated Human Sweat

Table 23A. *Static Test Results*

Sample No	Weight in Grams W0	W1	W2	W3	Reactivation Process	Weight Change in % α	β	γ
136	4.1550	5.2700	-	-	None	26.8	-	-
137	4.1300	5.2100	-	-	None	26.2	-	-
138	3.9350	5.0300	-	-	None	27.8	-	-
121	3.7282	*	-	4.5650	None	*	-	25.6
122	4.1094	*	-	5.0450	None	*	-	26.5
123	3.6794	*	-	4.6000	None	*	-	25.0
124	3.9741	*	-	4.9800	None	*	-	25.3
127	4.0800	5.1900	3.7400	4.9400	I/ ISO	27.2	-8.3	32.1
128	3.6000	4.5000	3.2888	4.2550	I/ ISO	25.0	-8.6	29.4
394	3.8950	4.9150	3.7126	4.7880	I/ ISO & MET	26.2	-4.7	29.0
395	4.0850	5.1450	3.9292	5.1800	I/ ISO & MET	26.0	-3.8	31.8
396	3.9652	4.9650	3.8150	5.0020	I/ ISO & MET & uW	25.2	-3.8	31.1

*CCl4 adsorption test omitted.

Table 23B. *Dynamic Test Results*

Sample No	Uncontaminated CCl_4 Flow mg/min	Uncontaminated Dynamic Adsorption Initial/Final mg/cm^2	Reactivation Process	Contaminated and Reactivated CCl_4 Flow mg/min	Contaminated and Reactivated Dynamic Adsorption Initial/Final mg/cm^2
136	*	*	NONE	16.3	1.86/2.04
137	*	*	NONE	17.5	1.75/1.86
138	*	*	NONE	14.7	1.49/1.65
121	*	*	NONE	16.0	1.78/2.05
122	*	*	NONE	16.0	2.24/2.72
123	*	*	NONE	16.0	1.87/2.19
124	*	*	NONE	16.1	1.87/2.14
127	*	*	I/ ISO	17.5	2.96/3.24
128	*	*	I/ISO	16.3	2.51/2.80
394	15.0	2.66/2.90	I/ ISO & MET	15.3	2.52/2.78
395	15.0	2.47/2.69	I/ ISO & MET	15.3	2.56/2.80
396	15.0	2.33/2.62	I/ ISO & MET & uW	15.1	2.30/2.56

* CCl_4 adsorption test omitted.

Based on data presented in Table 23, the following observations can be made:

(1) Samples 136, 137 and 138 were contaminated in simulated human sweat after a static CCl_4 adsorption test was performed. Apparently the difficulty associated with CCl_4 retention was reduced by immersion in an aqueous sweat solution.

(2) Sweat residues have a deleterious effect on the sorptive power of active carbon.

(3) Complete recovery of sorptive power was obtained with iodine/isopropanol wash plus methanol rinse or microwave activation. It is believed that water soluble sweat residues were removed in the aqueous wash phase used to remove iodine adsorption.

F. DISCUSSION: CONCLUSIONS FROM PHASE IIB

1. Method and procedure

In the present investigation, selected contaminants were separately applied to the test material in a controlled, reproducible manner. In order to assess the true efficacy of the reactivation process, efforts were made to apply each contaminant to the utmost extent, that is, in a manner far more severe than ever expected in real life to ensure full coverage, penetration, saturation and complete fouling by the contaminant.

It appears certain that the goal of complete reactivation of severely soiled active carbon foam material has been achieved. The contaminants whcih can be successfully removed include gasoline, diesel fuel, engine exhaust deposits, cigarette smoke residues and simulated human sweat. Even for foam samples severely soiled by diesel fuel, full recovery of the sorptive power in terms of both static and dynamic CCl_4 adsorption capabilities has been obtained.

The success of the reactivation process can be attributed to the following major factors:

(1) Use of iodine, a strong displacing agent for desorption of a broad spectrum of contaminants from active carbon, and a molecule of small diameter which can penetrate into micropores;

(2) Use of organic solvents into which the various contaminants are soluble;

(3) Use of low surface tension solvents which are capable of wetting surfaces, penetrating fine pores and getting between soils and the surfaces on which they are deposited and adsorbed;

(4) Use of methanol, a solvent proved to have low affinity for active carbon, as a special rinsing agent to eliminate solvent retention and the attendant poisoning effect on the carbon foam material;

(5) Use of ultrasonic excitation to induce microscopic solvent movement, to create a micro-mechanical solvent action from imploding and collapsing cavities and bubbles, without causing mechanical abrasion of the fabric or the impregnated carbon.

In Phase I and IIA, iodine was used in a solution containing 30% water and 70% isopropanol. This particular mixture was chosen in anticipation of encountering water soluble soils as well as solvent soluble contaminants. In retrospect, the introduction of water had rendered the solvent system ineffective. Because an adsorbate can be displaced only into a solvent in which it is soluble, soils such as diesel fuel and gasoline, which are water insoluble, may become trapped.

A more effective method was adopted where iodine was used in an organic solvent with which gasoline and diesel fuel are miscible. As a result, complete recovery of sorptive power was obtained even with such debilitating soils.

However, unlike the results found with aqueous systems, the application of a microwave field had no enhancing effect on dynamic sorption, when samples were dried in the microwave oven after they had been rinsed in methanol.

Therefore, an effective strategy for reactivating a chemical warfare protective fabric system that has emerged can be given by the following steps:

(1) Solvent wash cycle

The active carbon garment should be washed in a cold, iodine/organic solvent solution. In addition to the requirement of being able to dissolve various soils and contaminants, the solvent selected should also have a good solubility for iodine. In cases where there are a multitude of soils and contaminants such that two different solvents are required, the solvent wash should be conducted in a serial fashion as opposed to utilizing the solvents in a composite mixture.

(2) Methanol rinse cycle

After solvent wash, the garment should be rinsed in methanol in order to eliminate solvent retention and the attendant poisoning effect.

(3) Iodine removal cycle

After rinsing in methanol the garment is treated with an aqueous sodium thiosulfate solution followed by a tap water rinse cycle to remove sodium iodide, sodium tetrathionate and any unreacted sodium thiosulfate. If desired, laundry detergent, such as Type II nonphosphate detergent, can also be used to remove ordinary dirt and grime, which do not have any impact on the sorptive power of the active carbon garment.

(4) Supply retrieval cycle

The various solvents used can be reclaimed easily by using conventional techniques. If desired, iodine can also be recycled by a straightforward oxidation process.

(5) Other processes and cycles

There are also beneficial processes that can be incorporated in order to improve efficiency and effectiveness. These include ultrasonic excitation and vacuum evacuation.

In industrial dry cleaning, solvent blends instead of a pure solvent are frequently used to improve cleaning efficiency and power. As long as a particular soil is soluble in one of the component solvents, its removal is normally not seriously curtailed or hindered by the presence of ineffectual solvents. This is however not the case when a displacing agent is involved because the contaminant desorption is not spontaneous. The displacing agent is efficacious only when the contaminant is readily soluble in the solvent system. A typical example was given earlier regarding the removal of diesel fuel using an iodine solution consisting of 30 % water and 70 % isopropanol. Therefore, in the present application, a solvent mixture should be considered only if the potential

contaminant is soluble in all of its component solvents. Solvent blends are sometimes formulated to reduce fire hazard, and in these cases, azeotropic mixtures are preferred for ease of solvent reclamation and recycling.

Although Freon 113 is a better solvent for diesel fuel, the reactivation by iodine/Freon 113 system is consistently somewhat lower than that of iodine/isopropanol solution, due to the low solubility for iodine exhibited by Freon 113. (Unless residual Freon 113 is completely removed by a methanol rinse, it might be the cause of incomplete reactivation; the samples were allowed to dry after the wash in Freon 113, because it is not water-soluble, but Freon 113 might be harder to desorb than was the residual CCl_4 that remained after static tests.) It is believed that a mixture of Freon 113 and isopropanol or an azeotropic mixture of Freon 113 and methylene chloride (50-50 mixture) would be very effective due to the improved iodine solubility. These solvent blends are workable because diesel fuel is miscible with all three solvents mentioned.

2. Testing and evaluation

Certain potentially important restrictions to the application of the standard dynamic CCl_4 adsorption test[1b] were encountered in the Phase II-A study. It ws found that in the presence of certain contaminants such as gasoline, diesel fuel, cigarette smoke and engine exhaust, unrealistically long breaktimes were recorded. This anomaly was attributed to the existence of volatile residues, namely hydrocarbons, which interfere with the starch-iodide detection of pyrolyzed CCl_4[14,15].

Seemingly paradoxical enhancement in CCl_4 adsorption by the starch-iodide method was also observed in samples which underwent isopropanol wash. Again interference by the solvent residue was suspected. Despite the prolonged vacuum drying process at 50°C, a monolayer of isopropanol remained adsorbed. Since CCl_4 has a great affinity for active carbon, it may act as a displacing agent causing isopropyl alcohol molecules to desorb. These desorbed molecules, in turn, may prevent iodine in the bubbler solution from complexing with starch, and so the observed breaktime was lengthened artificially.

Because the presence of residues of both contaminants and solvents is an unavoidable reality especially for incompletely reactivated samples, the established dynamic vapor penetration test method based on pyrolyzer/bubbler assay was abandoned in the present study in favor of a flame assay technique. Essentially the modified apparatus (Fig. 12) uses a copper-halide flame sensor to detect penetrating CCl_4 vapor. Dry air instead of nitrogen is used as the carrier gas in order to sustain a constant propane flame. The distinctive green flame characteristic of the presence of chlorine atoms is not masked by the existence of any other species such as contaminants and solvents. The flame assay method was found to be invaluable for the present development.

In both standard and simplified dynamic vapor penetration tests, CCl_4 is used as an agent surrogate. There is sufficient evidence to show that CCl_4, due to its great affinity for active carbon, may act as a gaseous displacing agent for adsorbates present on the carbon surface. As a direct result, the sorptive power of the test sample may be overestimated because adsorbates, such as impurities, contaminants and solvent residues, are continuously desorbed and replaced by CCl_4 throughout the entire test period. However, it is believed that for reactivated test samples the sorptive power or dynamic adsorption determined in the present study is accurate and reliable largely due to the extra methanol rinse cycle, which eliminated solvent contamination.

VIII. THE SOLVENT AS DISPLACING AGENT, WITH ULTRASONIC EXCITATION

A. THE ULTRASONIC BATH DESIGN

For carbon foam material, conventional agitative laundering methods must be abandoned to avoid excessive carbon loss. Nonagitative cleaning can be achieved with great efficiency and efficacy by ultrasonic excitation. The various design parameters for a larger metal excitation tank were reviewed. The design is modularized with each transducer and the attendant excitation circuitry covering a localized zone. A large scale excitation tank can then be fabricated by assembling and installing a multitude of transducers and driving circuit modules.

Each transducer consists of a thin ceramic disc (2 inches in diameter and 0.1 inch thick) bonded to a similarly thin aluminum disc (3.5 inches in diameter). The metal disc is, in turn positioned against the external surfaces of the tank wall. The piezoelectric ceramic disc is made up of a hard PZT-4 crystal. PZT-4 is a lead zirconate titanate material capable of producing large mechanical drive amplitudes and intense ultrasound low losses. The transducer will be driven in the resonance mode at approximately 50 to 55 kHz. The radial vibration of the piezoelectric disc is transferred to the aluminum disc which supplies shear forces to the tank wall causing the wall to vibrate in a flexure mode and to radiate power into the liquid inside the tank. It is estimated that approximately 50 watts of power can be injected into each transducer for the excitation of a minimum of 1 gallon of liquid.

The ultrasonic power generator unit employs power transistors and transformers to form a power oscillator where the piezo-electric crystals mounted on the reactivation tank are used as the frequency determining network. With this design the proper oscillation frequency is always maintained, providing maximum ultrasonic power to the solvent contained in the tank. Current feedback is used to ensure the ultrasonic generator operates only at the low impedance resonant point of the driving crystals. Series and shunt inductors are also used to cancel any capacitive reaction present in the load (solvent and garment) so as to provide for maximum power deliverable to the transducer at all times.

B. FURTHER I_2/SOLVENT INVESTIGATIONS: FREON 123 AND METHYLENE CHLORIDE

Although isopropanol in conjunction with iodine effects recovery of the carbon sorptive power, a potentially superior operative system is anticipated with better oil solvents, such as Freon 123, or methylene chloride. Freon 123 was found to be miscible with gasoline, diesel fuel, and alcohols. Freon 123 (+90 = 213 --> $C_2H_1F_3CL_2$), a less stable substitute for Freon 113, should decompose well within the five years it would take to reach the stratosphere.

The affinity of Freon 123 for activated carbon was found to be much lower: 4.3% by weight after the 30-minute 50°C oven test (§VII.A.2), as against 27% for Freon 113 (Table 14). Both Freon 123 and methylene chloride are essentially nonflammable, yet have lower boiling point and latent heat of vaporization for economical solvent recovery. Methylene chloride has 1993 short term exposure limit STEL 100 ppm; it may be mutagenic according to tests on laboratory animals, and therefore is considered a possible carcinogen. Freon 123 has also been downgraded, to 10 ppm. The low boiling point of Freon 123, 27.6°C, would require special cooling, or mixing with higher- boiling solvent.

In our previous studies, water and methanol were found to be the only two solvents that have no affinity for active carbon. Methanol can be removed easily and entirely from the carbon foam material by simple vacuum evaporation. It is miscible with halocarbon solvents and has a low surface tension, so was chosen as an effective rinsing agent to alleviate or eliminate the poisoning effect of the particular solvent used for garment reactivation. With methanol as the last rinse of the reactivation process, heating is not necessary during the final drying of the

sample. The latent heat of liquid evaporation can be extracted from ambient by virtue of the lower boiling point of methanol.

Type III foam samples were contaminated with diesel fuel and subsequently reactivated with methylene chloride and iodine or Freon 123 and iodine. Although methylene chloride is moderately soluble in water, because of the previously observed affinity of methylene chloride for active carbon, the treated foam samples were subjected to a methanol rinse cycle following the reactivation process. Freon 123 is not soluble in water; therefore the iodine-treated samples were dried before aqueous steps were applied, and some samples were then rinsed with methanol. As expected for the high iodine concentration supported by methylene chloride, full recovery of the sorptive power was achieved with this solvent. Freon 123 did not produce complete recovery, and lower iodine solubility in Freon 123 was assumed to be the cause of incomplete reactivation. However, reactivation by methylene chloride was later accomplished without iodine, see below, suggesting that the lower iodine solubility in Freon 123 is also a symptom of its lower solvent affinity for activated carbon, and lower displacement potential.

C. 100% REACTIVATION WITHOUT IODINE, IN SOLVENT SEQUENCE

Extensive studies were performed to explore the possibility of achieving the same performance without using iodine and the attendant processes. It was believed that by prolonging the ultrasonic excitation time and with a large solvent volume, complete recovery of sorptive capacity could be attained, even without iodine. It was necessary to eliminate plastic ware from the procedure, as both Freon 123 and methylene chloride dissolve Lucite™ (acrylic), Lexan™ (polycarbonate), ABS, polystyrene, ethylcellulose, etc.

The controlled contamination procedures and the ultrasonic bath reactivation steps, except for the use of iodine and concomitant aqueous rinses, were applied to Type III foam. Samples which were heavily soiled with diesel fuel, gasoline, cigarette smoke, engine exhaust, or simulated human sweat, were completely restored to original activity by methylene chloride, without resorting to iodine. For removal of gasoline or diesel fuel from saturated clothing samples, two 30 minute cycles in the methylene chloride ultrasonic bath, followed by methanol rinse for two 5-minute cycles in ultrasonic bath, were used. Lesser soils required fewer cycles. Methylene chloride has the tendency to swell the foam material appreciably. However, the swelling subsided when methanol was introduced for the rinsing cycles.

Despite carbon loss of up to 10% by weight (of activated carbon (AC)/foam sample) the sorptive power after reactivation is completely recovered or even improved, in several cases. Results are collected in Table 24. The methanol-rinsed AC/foams were not dried with heat, and they show enhanced sorptivity. Tests on these samples performed several months later when the automated FTIR CCl_4 vapor test apparatus became available, are also shown in Table 24. The later tests were done after oven-drying the samples, and no enhancement is found. The behavior is reminiscent of that of water-moist samples of AC-impregnated foam, which show 10-20% enhancement relative to oven-dried samples. A number of the reactivated samples of Table 24 had been soaked in trichloroethylene overnight and regenerated before retesting in the FTIR Dawson apparatus. There was no change in sample weight, and no loss of impregnated carbon, despite great swelling of the foam in this solvent, and there appears to be no effect on sorptivity.

Table 24. Cleaning and Reactivation of Soiled CP Liner (AC/Foam) In Ultrasonic Baths of Methylene Chloride and Methanol

TREATMENT soil/ reactivation	Sample no.	CCl_4 Vapor adsorption (mg/sq cm) FRESH (mg/sq cm) Cu-flame	REACTIVATED Cu-flame	REACTIVATED FTIR*	Sorptivity ratio Reactivated/Fresh Cu-flame	Sorptivity ratio Reactivated/Fresh FTIR*
Cigarette smoke/ 2xMeOH	B11	3.02	3.33	2.62	1.10	0.87
	B12	3.11	3.60	2.89	1.16	0.93
	B13	3.25	4.33	2.90	1.33	0.89
	B14	2.91	2.88	2.29	0.99	0.79
Sweat/ 3xMeOH	B59	3.41	4.01	3.71	1.18	1.08
	B60	3.17	3.83	3.45	1.21	1.09
Diesel fuel/ 4xMeCl2	B23	3.23	0	2.12	--	0.66
Gasoline fumes/ 1xMeCl2,3xMeOH	90	3.42	4.02	3.08	1.17	0.90
	95	3.44	4.42	2.72	1.28	0.79
	96	2.96	3.08	2.49	1.04	0.84
Diesel fumes/ 1xMeCl2,3xMeOH	B52	3.46	4.24	3.56	1.22	1.03
	B53	2.96	3.54	3.38	1.19	1.14
Diesel fumes/ 1xi-propnol,3xMeOH	B54	3.38	2.54	2.91	0.75	0.86
Gasoline/ 2xMeCl2,2xMeOH	B27	3.31	4.09	2.87	1.23	0.87
	B28	3.09	3.68	3.09	1.19	1.00
Diesel fuel/ 2xMeCl2,2xMeOH	B117	2.98	3.45	2.87	1.16	0.96
	B118	2.90	3.08	2.86	1.06	0.99
None	D11	3.49		2.12		0.61
	D12	3.47		1.96		0.56

*Stored several months.

Note that after being CCl_4 - tested, the two untreated control samples have lost sorptivity after oven regeneration and storage for several months.

Underlined values are trichloroethylene-soaked samples, dried 48 h in 95 °C airflow oven.

Conclusions that may be drawn from the data of Table 24 are as follows:

(1) Sweat can be removed with methanol alone, but smoke and diesel fumes leave a residue.

(2) Methylene chloride completely removes diesel fumes in one cycle, but leaves a residue from gasoline fumes. (Gasoline contains 40% aromatics, diesel fuel contains 2-20%; two-ring aromatics have high GC retention[19].) Removal of diesel fuel and gasoline is complete after two (30 minute) methylene chloride cycles.

(3) Methylene chloride is not all removed from activated carbon by oven-drying; rinsing with methanol is necessary to prevent loss of sorptivity.

(4) The loss of sorptivity by unsoiled, control samples, several months after tests with CCl_4, is typical behavior. Activated carbon samples that had been tested with alkyl halide vapors retained reacted Cl after standing in air before high heat and vacuum regeneration[20], and Natick studies have shown that repeatedly CCl_4-tested samples, regenerated in an airflow oven above the boiling point, gradually lose appreciable sorptive activity over time, irreversibly[21]. Evidently reaction between CCl_4 and graphite, which also involves moisture, had not yet taken place when freshly CCl_4-tested samples were promptly soiled and reactivated by the methods that included cycles of methanol rinse. Only the unreactivated control samples, or the sample that was not rinsed with methanol after $MeCl_2$ (B23) show large deterioration in sorptive action. Methanol removes trace alkyl halide from activated carbon, if promptly applied; however once activity has deteriorated, methanol has no effect on the C-Cl-H_2O reaction product that irreversibly reduces sorptivity[18b].

(5) The 10-20% higher sorptivity found after ambient drying of methanol-rinsed reactivated samples parallels the observations on water-wetted activated carbon/foam, which was ascribed to the effect of polymer restructuring[14] to expose greater adsorptive surface.

IX. CONCLUSIONS AND RECOMMENDATIONS

A. CONCLUSIONS: THERE ARE TWO SUCCESSFUL REACTIVATION METHODS

1. Iodine displacement in organic solvent

In an ultrasonic bath, all soils are removed from activated carbon material by the iodine in pure isopropanol solution. Aqueous thiosulfate rinse to remove iodine, and water rinse, must still be followed by a rinse step with methanol, to remove residual isopropanol, all in ultrasonic baths.

2. Methylene chloride displacement

All soils are removed from activated carbon material in two 30 minute methylene chloride ultrasonic bath cycles, followed by two 5 minute cycles in methanol to remove methylene chloride.

The second method requires only two solvents and has low-temperature solvent reclamation capabilities; it is, therefore, the recommended method for scale-up to an Army Reactivation System, for nondestructive reactivation of chemical protective garments and wraps.

B. RECOMMENDATIONS: A REACTIVATION UNIT

Recommendation 1. The proposed Army Reactivation System features nonagitative solvent flow around stationary garments hung on racks, and separated from one another by transducer-assembly plates that provide ultrasonic solvent micro-pulse washing action. Thirty-two jacket or trouser garments with nine transducer assembly plates are estimated to fill one third of the volume of an eight-compartment tank, 64x48x44 cu in. The remaining volume to be filled with liquid is 390 gallons. A truck and trailer are needed for transport of the tank, solvent drums, solvent recovery stills and coolers. A sketch of such a system is shown in Figure 15.

Optical detectors indicate the extent of contamination in the $MeCl_2$ solvent. Solvent replacement can be done on demand, that is, when effluent shows high density. Trials will show whether the longer time required to operate the compartments independently of each other for washing is outweighed by the smaller solvent volume that would be needed. In any case, rinsing could be done sequentially, solvent passing from one compartment to the next. The first prototype would have the compartments isolated from each other for this purpose.

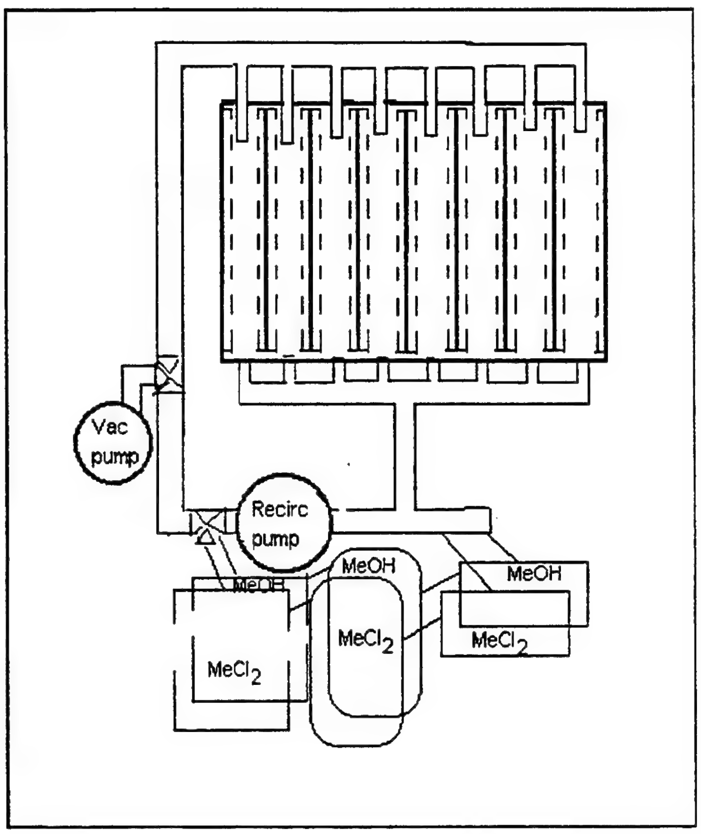


Figure 15. Diagram of ultrasonic unit for methylene chloride reactivation of AC garments

Recommendation 2. Coordination: intercourse among Army centers and directorates that are developing LADDS, NAEDS[22], and other drycleaning, laundering, and decontamination projects, is recommended to expedite the development of a dry-cleaning system that can reactivate chemical protective fabrics. Requirements of the proposed unit, such as restriction to metal and teflon materials, large solvent volume, sequence of two solvents, containment of vapors, transducer plates, and compartmented tank, demand innovative approaches; similar requirements to those already in use, such as power generation, solvent recycling/distillation, transport, require combinations of expertise.

Recommendation 3. Assembly of a one-quarter size, nonmobile prototype, with tube connections between tank and solvent recovery system, and automation of the complete process insofar as a continuous solvent flow, two-solvent sequencing, solvents recovery, and evacuation drying is involved.

X. REFERENCES

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b. *Ibid.,* 4.5.2, p.14.

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